

## Section IV

### ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

5 Organic molecules comprising an arbitrary number of atoms can be solved using the similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of  $CH_3$ ,  $CH_2$ , and  $C - C$ . These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes  
10 section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkynes, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides,  
15 urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfones, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by  
20 using generalized forms of the geometrical and energy equations. The equations and sections that are referenced by not contained in this text refer to those sections and equations of the book by R. L. Mills entitled, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at  
25 <http://www.blacklightpower.com/bookdownload.shtml> which is incorporated in its entirety by reference.

Consider the case wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO  
30 permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force generalized constant  $k'$  of a



$H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\epsilon_0} \quad (15.1)$$

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of  $H$  bonding to a central atom and 0.5 (Eq. (14.152)) otherwise, and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus  $c'$  is given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}} \quad (15.2)$$

10 The internuclear distance is

$$2c' = 2 \sqrt{\frac{aa_0}{2C_1 C_2}} \quad (15.3)$$

The length of the semiminor axis of the prolate spheroidal MO  $b = c$  is given by

$$b = \sqrt{a^2 - c'^2} \quad (15.4)$$

And, the eccentricity,  $e$ , is

$$15 \quad e = \frac{c'}{a} \quad (15.5)$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (15.6)$$

The potential energy of the two nuclei is

$$20 \quad V_p = n_1 \frac{e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \quad (15.7)$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (15.8)$$

And, the energy,  $V_m$ , of the magnetic force between the electrons is



$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (15.9)$$

The total energy of the  $H_2$ -type prolate spheroidal MO,  $E_T(H_2MO)$ , is given by the sum of the energy terms:

$$E_T(H_2MO) = V_e + T + V_m + V_p \quad (15.10)$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] \\ &= -\frac{n_1 e^2}{8\pi\epsilon_0 c'} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \end{aligned} \quad (15.11)$$

where  $n_1$  is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules, and 9 for an independent triplet bond. Then, the kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond.  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of  $H$  bonding to an unhybridized central atom and 1 otherwise, and  $c_2$  is the factor that results in an equipotential energy match of the participating the MO and the at least two atomic orbitals of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the  $H_2$ -type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of  $H$ , (iii) the ratio of the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two  $c_2$  factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different  $c_2$  factors corresponding to any of the cases (i)-(v). Specific examples of the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO given in previous sections are

0.936127, the ratio of the ionization energy of  $N$  14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of  $H$ ;



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0.91771, the ratio of 14.82575 eV,  $-E_{Coulomb}(C, 2sp^3)$ , and 13.605804 eV ;

0.87495, the ratio of 15.55033 eV,  $-E_{Coulomb}(C_{ethane}, 2sp^3)$ , and 13.605804 eV ;

0.85252, the ratio of 15.95955 eV,  $-E_{Coulomb}(C_{ethylene}, 2sp^3)$ , and 13.605804 eV ;

0.85252, the ratio of 15.95955 eV,  $-E_{Coulomb}(C_{benzene}, 2sp^3)$ , and 13.605804 eV, and

5 0.86359, the ratio of 15.55033 eV,  $-E_{Coulomb}(C_{alkane}, 2sp^3)$ , and 13.605804 eV .

In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for  
10 each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy  $E_T(atom, msp^3)$  ( $m$  is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the  $n$  electrons comprising total electrons of the at least one AO shell.

$$15 \quad E_T(atom, msp^3) = -\sum_{m=1}^n IP_m \quad (15.12)$$

where  $IP_m$  is the  $m$ th ionization energy (positive) of the atom. The radius  $r_{msp^3}$  of the hybridized shell is given by:

$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{-(Z-q)e^2}{8\pi\epsilon_0 E_T(atom, msp^3)} \quad (15.13)$$

Then, the Coulombic energy  $E_{Coulomb}(atom, msp^3)$  of the outer electron of the  $atom msp^3$   
20 shell is given by

$$E_{Coulomb}(atom, msp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{msp^3}} \quad (15.14)$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(magnetic)$  at the initial radius  $r$  of the AO electron:

$$25 \quad E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = \frac{8\pi\mu_0 \mu_B^2}{r^3} \quad (15.15)$$



Then, the energy  $E(atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell is given by the sum of  $E_{Coulomb}(atom, msp^3)$  and  $E(magnetic)$ :

$$E(atom, msp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} \quad (15.16)$$

Consider next that the at least two atomic orbitals hybridize as a linear combination of 5 electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the 10 hybridized orbitals is given by the sum of  $E(atom, msp^3)$  and the next energies of successive ions of the atom over the  $n$  electrons comprising the total electrons of the at least two initial AO shells. Here,  $E(atom, msp^3)$  is the sum of the first ionization energy of the atom and the hybridization energy. An example of  $E(atom, msp^3)$  for  $E(C, 2sp^3)$  is given in Eq. (14.503) where the sum of the negative of the first ionization energy of  $C$ ,  $-11.27671 \text{ eV}$ , plus the 15 hybridization energy to form the  $C2sp^3$  shell given by Eq. (14.146) is  $E(C, 2sp^3) = -14.63489 \text{ eV}$ .

Thus, the sharing of electrons between two  $atom msp^3$  HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each  $atom msp^3$  20 HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total 25 Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy  $E_T(mol.atom, msp^3)$  ( $m$  is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the  $n$  electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:



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$$E_T(\text{mol.atom}, msp^3) = E(\text{atom}, msp^3) - \sum_{m=2}^n IP_m \quad (15.17)$$

where  $IP_m$  is the  $m$ th ionization energy (positive) of the atom and the sum of  $-IP_1$  plus the hybridization energy is  $E(\text{atom}, msp^3)$ . Thus, the radius  $r_{msp^3}$  of the hybridized shell is given by:

$$5 \quad r_{msp^3} = \left( \sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25) \right) \frac{-e^2}{8\pi\epsilon_0 E_T(\text{mol.atom}, msp^3)} \quad (15.18)$$

where  $s = 1, 2, 3$  for a single, double, and triple bond, respectively. The Coulombic energy  $E_{Coulomb}(\text{mol.atom}, msp^3)$  of the outer electron of the  $\text{atom } msp^3$  shell is given by

$$E_{Coulomb}(\text{mol.atom}, msp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{msp^3}} \quad (15.19)$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(\text{magnetic})$  at the initial radius  $r$  of the AO electron given by Eq. (15.15). Then, the energy  $E(\text{mol.atom}, msp^3)$  of the outer electron of the  $\text{atom } msp^3$  shell is given by the sum of  $E_{Coulomb}(\text{mol.atom}, msp^3)$  and  $E(\text{magnetic})$ :

$$E(\text{mol.atom}, msp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} \quad (15.20)$$

15  $E_T(\text{atom} - \text{atom}, msp^3)$ , the energy change of each  $\text{atom } msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(\text{mol.atom}, msp^3)$  and  $E(\text{atom}, msp^3)$ :

$$E_T(\text{atom} - \text{atom}, msp^3) = E(\text{mol.atom}, msp^3) - E(\text{atom}, msp^3) \quad (15.21)$$

As examples from prior sections,  $E_{Coulomb}(\text{mol.atom}, msp^3)$  is one of:

$$20 \quad E_{Coulomb}(C_{\text{ethylene}}, 2sp^3), \quad E_{Coulomb}(C_{\text{ethane}}, 2sp^3), \quad E_{Coulomb}(C_{\text{acetylene}}, 2sp^3), \quad \text{and} \\ E_{Coulomb}(C_{\text{alkane}}, 2sp^3);$$

$E_{Coulomb}(\text{atom}, msp^3)$  is one of  $E_{Coulomb}(C, 2sp^3)$  and  $E_{Coulomb}(Cl, 3sp^3)$ ;



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$E(\text{mol.atom}, msp^3)$  is one of  $E(C_{ethylene}, 2sp^3)$ ,  $E(C_{ethane}, 2sp^3)$ ,  $E(C_{acetylene}, 2sp^3)$ ,  $E(C_{alkane}, 2sp^3)$ ;

$E(\text{atom}, msp^3)$  is one of and  $E(C, 2sp^3)$  and  $E(Cl, 3sp^3)$ ;

$E_T(\text{atom} - \text{atom}, msp^3)$  is one of  $E(C - C, 2sp^3)$ ,  $E(C = C, 2sp^3)$ , and  $E(C \equiv C, 2sp^3)$ ;

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$\text{atom } msp^3$  is one of  $C2sp^3$ ,  $Cl3sp^3$

$E_T(\text{atom} - \text{atom}(s_1), msp^3)$  is  $E_T(C - C, 2sp^3)$  and  $E_T(\text{atom} - \text{atom}(s_2), msp^3)$  is  $E_T(C = C, 2sp^3)$ , and

$r_{msp^3}$  is one of  $r_{C2sp^3}$ ,  $r_{ethane2sp^3}$ ,  $r_{ethylene2sp^3}$ ,  $r_{acetylene2sp^3}$ ,  $r_{alkane2sp^3}$ , and  $r_{Cl3sp^3}$ .

In the case of the  $C2sp^3$  HO, the initial parameters (Eqs. (14.142-14.146)) are

$$10 \quad r_{2sp^3} = \sum_{n=2}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0 (e148.25751 \text{ eV})} = \frac{10e^2}{8\pi\epsilon_0 (e148.25751 \text{ eV})} = 0.91771a_0 \quad (15.22)$$

$$E_{Coulomb}(C, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.91771a_0} = -14.82575 \text{ eV} \quad (15.23)$$

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \text{ eV} \quad (15.24)$$

$$\begin{aligned} E(C, 2sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} \\ &= -14.82575 \text{ eV} + 0.19086 \text{ eV} \\ &= -14.63489 \text{ eV} \end{aligned} \quad (15.25)$$

In Eq. (15.18),

$$15 \quad \sum_{q=Z-n}^{Z-1} (Z-q) = 10 \quad (15.26)$$

Eqs. (14.147) and (15.17) give

$$E_T(\text{mol.atom}, msp^3) = E_T(C_{ethane}, 2sp^3) = -151.61569 \text{ eV} \quad (15.27)$$

Using Eqs. (15.18-15.28), the final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$ , and the resulting  $E_T(C - C, C2sp^3)$  of the MO due to charge donation from the HO to the MO where



$C-C$  refers to the bond order of the carbon-carbon bond for different values of the parameter  $s$  are given in Table 15.1.

Table 15.1. The final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$  and the resulting  $E_T(C-C, C2sp^3)$  of the MO due to charge donation from the HO to the MO where  $C-C$  refers to the bond order of the carbon-carbon bond.

MO Bond Order (BO)	$s$ 1	$s$ 2	$r_{C2sp^3}(a_0)$ Final	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$E_T(C-C, C2sp^3)$ (eV)
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
II	2	0	0.85252	-15.95955	-15.76868	-1.13379
III	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell of each bonding atom must be the average of  $E(mol.atom, msp^3)$  for two different values of  $s$ :

$$E(mol.atom, msp^3) = \frac{E(mol.atom(s_1), msp^3) + E(mol.atom(s_2), msp^3)}{2} \quad (15.28)$$

In this case,  $E_T(atom - atom, msp^3)$ , the energy change of each  $atom msp^3$  shell with the formation of each atom-atom-bond MO, is average for two different values of  $s$ :

$$E_T(atom - atom, msp^3) = \frac{E_T(atom - atom(s_1), msp^3) + E_T(atom - atom(s_2), msp^3)}{2} \quad (15.29)$$

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each  $C=C$  double bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each  $C-H$  bond of  $CH$  having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the



linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO as given by Eq. (13.439). However,  $E_T(atom - atom, msp^3)$  of the  $C-H$ -bond MO is given by  $0.5E_T(C = C, 2sp^3)$  (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for  $C-H$  that is lowered in energy due to the aromatic  
5 character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of  $H_2$ -type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75,  
10 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO  
15 comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general,  $E_T(atom - atom, msp^3)$ , the energy change of each  $atom msp^3$  shell with the formation of  
20 each atom-atom-bond MO, is a weighted linear sum for different values of  $s$  that matches the energy of the bonded MOs, HOs, and AOs:

$$E_T(atom - atom, msp^3) = \sum_{n=1}^N c_{s_n} E_T(atom - atom(s_n), msp^3) \quad (15.30)$$

where  $c_{s_n}$  is the multiple of the BO of  $s_n$ . The radius  $r_{msp^3}$  of the  $atom msp^3$  shell of each bonding atom is given by the Coulombic energy using the initial energy  $E_{Coulomb}(atom, msp^3)$   
25 and  $E_T(atom - atom, msp^3)$ , the energy change of each  $atom msp^3$  shell with the formation of each atom-atom-bond MO:

$$r_{msp^3} = \frac{-e^2}{8\pi\epsilon_0\alpha_0 (E_{Coulomb}(atom, msp^3) + E_T(atom - atom, msp^3))} \quad (15.31)$$



where  $E_{Coulomb}(C2sp^3) = -14.825751 \text{ eV}$ . The Coulombic energy  $E_{Coulomb}(mol.atom,msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(magnetic)$  (Eq. (15.15)) at the initial radius  $r$  of the AO electron. Then, the energy  $E(mol.atom,msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Coulomb}(mol.atom,msp^3)$  and  $E(magnetic)$  (Eq. (15.20)).  $E_T(atom - atom,msp^3)$ , the energy change of each  $atom\ msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom,msp^3)$  and  $E(atom,msp^3)$  given by Eq. (15.21). Using Eq. (15.23) for  $E_{Coulomb}(C,2sp^3)$  in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

Table 15.2. The final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$  and the resulting  $E_T\left(\overset{BO}{C} - C, C2sp^3\right)$  of the MO comprising a linear combination of  $H_2$ -type ellipsoidal MOs and corresponding HOs of single or mixed bond order where  $c_{s_n}$  is the multiple of the bond order parameter  $E_T(atom - atom(s_n),msp^3)$  given in Table 15.1.



Table 15.1

MO Bond Order (BO)	$s$ 1	$c_{s_1}$	$s$ 2	$c_{s_2}$	$s$ 3	$c_{s_3}$	$r_{C2sp^3}(a_0)$ Final	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$E_T\left(C - C, C2sp^3\right)$ (eV)
1/2I	1	0.5	0	0	0	0	0.89582	-15.18804	-14.99717	-0.36228
1/2II	2	0.5	0	0	0	0	0.88392	-15.39265	-15.20178	-0.56689
I +	1	0.5	2	0.2	0	0	0.87941	-15.47149	-15.28062	-0.64573
1/2II				5						
1/2II	2	0.2	1	0.2	2	0.2	0.87363	-15.57379	-15.38293	-0.74804
+ (I + II)		5		5		5				
3/4II	2	0.7	0	0	0	0	0.86793	-15.67610	-15.48523	-0.85034
		5								
I + II	1	0.5	2	0.5	0	0	0.86359	-15.75493	-15.56407	-0.92918
I +	1	0.5	3	0.5	0	0	0.85193	-15.97060	-15.77974	-1.14485
III										
I +	1	0.5	4	0.5	0	0	0.83995	-16.19826	-16.00739	-1.37250
IV										
II +	2	0.5	3	0.5	0	0	0.84115	-16.17521	-15.98435	-1.34946
III										
II +	2	0.5	4	0.5	0	0	0.82948	-16.40286	-16.21200	-1.57711
IV										
III +	3	0.5	4	0.5	0	0	0.81871	-16.61853	-16.42767	-1.79278
IV										
IV +	4	0.5	4	0.5	0	0	0.80765	-16.84619	-16.65532	-2.02043
IV										

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as 5 carbon superimposes linearly. In general, the radius  $r_{mol2sp^3}$  of the  $C2sp^3$  HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering  $\sum E_{T_{mol}}(MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by



$$\begin{aligned}
 r_{mol2sp^3} &= \frac{-e^2}{8\pi\epsilon_0 \left( E_{Coulomb}(C, 2sp^3) + \sum E_{T_{mol}}(MO, 2sp^3) \right)} \\
 &= \frac{e^2}{8\pi\epsilon_0 \left( e14.825751 \text{ eV} + \sum |E_{T_{mol}}(MO, 2sp^3)| \right)}
 \end{aligned}
 \tag{15.32}$$

The Coulombic energy  $E_{Coulomb}(mol.atom, msp^3)$  of the outer electron of the *atom msp<sup>3</sup>* shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(magnetic)$  (Eq. (15.15)) at the initial radius  $r$  of the AO electron. Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the *atom msp<sup>3</sup>* shell is given by the sum of  $E_{Coulomb}(mol.atom, msp^3)$  and  $E(magnetic)$  (Eq. (15.20)).

For example, the  $C2sp^3$  HO of each methyl group of an alkane contributes  $-0.92918 \text{ eV}$  (Eq. (14.513)) to the corresponding single  $C-C$  bond; thus, the corresponding  $C2sp^3$  HO radius is given by Eq. (14.514). The  $C2sp^3$  HO of each methylene group of  $C_nH_{2n+2}$  contributes  $-0.92918 \text{ eV}$  to each of the two corresponding  $C-C$  bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

$$\begin{aligned}
 r_{alkaneC_{methylene}2sp^3} &= \frac{-e^2}{8\pi\epsilon_0 \left( E_{Coulomb}(C, 2sp^3) + \sum E_{T_{alkane}}(methylene\ C-C, 2sp^3) \right)} \\
 &= \frac{e^2}{8\pi\epsilon_0 (e14.825751 \text{ eV} + e0.92918 \text{ eV} + e0.92918 \text{ eV})} \\
 &= 0.81549a_0
 \end{aligned}
 \tag{15.33}$$

$$E_{Coulomb}(C_{methylene}2sp^3) = \frac{-e^2}{8\pi\epsilon_0 (0.81549a_0)} = -16.68412 \text{ eV}
 \tag{15.34}$$

$$E(C_{methylene}2sp^3) = \frac{-e^2}{8\pi\epsilon_0 (0.81549a_0)} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (0.84317a_0)^3} = -16.49325 \text{ eV}
 \tag{15.35}$$

In the determination of the parameters of functional groups, heteroatoms bonding to  $C2sp^3$  HOs to form MOs are energy matched to the  $C2sp^3$  HOs. Thus, the radius and the energy parameters of a bonding heteroatom are given by the same equations as those for



$C2sp^3$  HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO,  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}(mol.atom,msp^3)$ , and  $E(C_{mol}2sp^3)$  are calculated using  $\sum E_{T_{group}}(MO,2sp^3)$ , the total energy donation to each bond with which an atom participates in bonding corresponding to the values of  $E_T\left(C^{BO}-C,C2sp^3\right)$  of

5 the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}(mol.atom,msp^3)$ , and  $E(C_{mol}2sp^3)$  calculated using the values of  $E_T\left(C^{BO}-C,C2sp^3\right)$  given in Tables 15.1 and 15.2.



Atom Hybridiz ation Designat ion	$E_r \left( C - C, C2sp^3 \right)^{BO}$	$E_r \left( C - C, C2sp^3 \right)^{BO}$	$E_r \left( C - C, C2sp^3 \right)^{BO}$	$E_r \left( C - C, C2sp^3 \right)^{BO}$	$E_r \left( C - C, C2sp^3 \right)^{BO}$	$r_{Atom, HO, AO}$ Final	$E_{Condonb} (mol\ atom, msp^3)$ (eV) Final	$E(C_{and} 2sp^3)$ (eV) Final
1	0	0	0	0	0	0.91771	-14.82575	-14.63489
2	-0.36229	0	0	0	0	0.89582	-15.18804	-14.99717
3	-0.46459	0	0	0	0	0.88983	-15.29034	-15.09948
4	-0.56689	0	0	0	0	0.88392	-15.39265	-15.20178
5	-0.72457	0	0	0	0	0.87495	-15.55033	-15.35946
6	-0.85034	0	0	0	0	0.86793	-15.6761	-15.48523
7	-0.92918	0	0	0	0	0.86359	-15.75493	-15.56407
8	-0.54343	-0.54343	0	0	0	0.85503	-15.91261	-15.72175
9	-1.13379	0	0	0	0	0.85252	-15.95955	-15.76868
10	-1.14485	0	0	0	0	0.85193	-15.9706	-15.77974
11	-0.46459	-0.82688	0	0	0	0.84418	-16.11722	-15.92636
12	-1.34946	0	0	0	0	0.84115	-16.17521	-15.98435
13	-1.3725	0	0	0	0	0.83995	-16.19826	-16.00739
14	-0.46459	-0.92918	0	0	0	0.83885	-16.21952	-16.02866
15	-0.72457	-0.72457	0	0	0	0.836	-16.2749	-16.08404
16	-0.5669	-0.92918	0	0	0	0.8336	-16.32183	-16.13097
17	-0.82688	-0.72457	0	0	0	0.83078	-16.37721	-16.18634
18	-1.56513	0	0	0	0	0.83008	-16.39089	-16.20002
19	-0.64574	-0.92918	0	0	0	0.82959	-16.40067	-16.20981
20	-1.57711	0	0	0	0	0.82948	-16.40286	-16.212
21	-0.72457	-0.92918	0	0	0	0.82562	-16.47951	-16.28865
22	-0.85035	-0.85035	0	0	0	0.82327	-16.52645	-16.33559
23	-1.79278	0	0	0	0	0.81871	-16.61853	-16.42767
24	-1.13379	-0.72457	0	0	0	0.81549	-16.68411	-16.49325
25	-0.92918	-0.92918	0	0	0	0.81549	-16.68412	-16.49325
26	-2.02043	0	0	0	0	0.80765	-16.84619	-16.65532



27	-1.13379	-0.92918	0	0	0	0.80561	-16.88872	-16.69786
28	-0.85035	-0.85035	-0.46459	0	0	0.80076	-16.99104	-16.80018
29	-0.5669	-0.72457	-0.92918	0	0	0.78916	-17.04641	-16.85554
30	-1.13379	-1.13379	0	0	0	0.79597	-17.09334	-16.90248
31	-1.34946	-0.92918	0	0	0	0.79546	-17.1044	-16.91353
32	-0.46459	-0.92918	-0.92918	0	0	0.79340	-17.14871	-16.95784
33	-0.64574	-0.85034	-0.85034	0	0	0.79232	-17.17217	-16.98131
34	-0.85035	-0.5669	-0.92918	0	0	0.79232	-17.17218	-16.98132
35	-0.72457	-0.72457	-0.92918	0	0	0.79085	-17.20408	-17.01322
36	-0.82688	-0.72457	-0.92918	0	0	0.78617	-17.30638	-17.11552
37	-0.72457	-0.92918	-0.92918	0	0	0.78155	-17.40868	-17.21782
38	-0.92918	-0.72457	-0.92918	0	0	0.78155	-17.40869	-17.21783
39	-0.54343	-0.54343	-0.5669	-0.92918	0	0.78155	-17.40869	-17.21783
40	-0.92918	-0.85034	-0.85034	0	0	0.77945	-17.45561	-17.26475
41	-0.82688	-0.92918	-0.92918	0	0	0.77699	-17.51099	-17.32013
42	-0.92918	-0.92918	-0.92918	0	0	0.77247	-17.6133	-17.42244
43	-0.85035	-0.54343	-0.5669	-0.92918	0	0.76801	-17.71561	-17.52475
44	-1.34946	-0.64574	-0.92918	0	0	0.76652	-17.75013	-17.55927
45	-0.85034	-0.54343	-0.60631	-0.92918	0	0.76631	-17.75502	-17.56415
46	-1.1338	-0.92918	-0.92918	0	0	0.7636	-17.81791	-17.62705
47	-0.46459	-0.85035	-0.85035	-0.92918	0	0.75924	-17.92022	-17.72936
48	-0.82688	-1.34946	-0.92918	0	0	0.75877	-17.93128	-17.74041
49	-1.13379	-1.13379	-1.13379	0	0	0.74646	-18.22712	-18.03626
50	-1.79278	-0.92918	-0.92918	0	0	0.73637	-18.47690	-18.28604



Table 15.3.B. The final values of  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}(mol.atom,msp^3)$ , and  $E(C_{mol}2sp^3)$  calculated for heterocyclic groups using the values of  $E_T\left(C^{bo}-C,C2sp^3\right)$  given in Tables 15.1 and 15.2.



Atom Hybridization Designation	$E_i \left( C - C, C2sp^3 \right)$	$E_i \left( C - C, C2sp^3 \right)$	$E_i \left( C - C, C2sp^3 \right)$	$E_i \left( C - C, C2sp^3 \right)$	$E_i \left( C - C, C2sp^3 \right)$	$r_{Atom, HO, AO}$ Final	$E_{coulomb} (mol, atom, msp^3)$ (eV) Final	$E(C_{mol} 2sp^3)$ (eV) Final
1	0	0	0	0	0	0.91771	-14.82575	-14.63489
2	-0.56690	0	0	0	0	0.88392	-15.39265	-15.20178
3	-0.72457	0	0	0	0	0.87495	-15.55033	-15.35946
4	-0.92918	0	0	0	0	0.86359	-15.75493	-15.56407
5	-0.54343	-0.54343	0	0	0	0.85503	-15.91261	-15.72175
6	-1.13379	0	0	0	0	0.85252	-15.95954	-15.76868
7	-0.60631	-0.60631	0	0	0	0.84833	-16.03838	-15.84752
8	-0.46459	-0.92918	0	0	0	0.83885	-16.21953	-16.02866
9	-0.72457	-0.72457	0	0	0	0.83600	-16.27490	-16.08404
10	-0.92918	-0.60631	0	0	0	0.83159	-16.36125	-16.17038
11	-0.92918	-0.72457	0	0	0	0.82562	-16.47951	-16.28864
12	-0.85035	-0.85035	0	0	0	0.82327	-16.52644	-16.33558
13	-0.92918	-0.92918	0	0	0	0.81549	-16.68411	-16.49325
14	-1.13379	-0.72457	0	0	0	0.81549	-16.68412	-16.49325
15	-1.13379	-0.92918	0	0	0	0.80561	-16.88873	-16.69786
16	-0.85035	-0.85035	-0.46459	0	0	0.80076	-16.99103	-16.80017
17	-0.85034	-0.85034	-0.56690	0	0	0.79597	-17.09334	-16.90247
18	-1.13379	-1.13380	0	0	0	0.79597	-17.09334	-16.90248
19	-0.85035	-0.54343	0.00000	-0.92918	0	0.79340	-17.14871	-16.95785
20	-0.85035	-0.56690	-0.92918	0	0	0.79232	-17.17218	-16.98132
21	-0.54343	-0.54343	-0.56690	-0.92918	0	0.78155	-17.40869	-17.21783
22	-0.85034	-0.28345	-0.54343	-0.92918	0	0.78050	-17.43216	-17.24130
23	-0.92918	-0.92918	-0.92918	0	0	0.77247	-17.61330	-17.42243
24	-0.85034	-0.54343	-0.56690	-0.92918	0	0.76801	-17.71560	-17.52474
25	-0.85034	-0.54343	-0.60631	-0.92918	0	0.76631	-17.75502	-17.56416
26	-1.13379	-0.92918	-0.92918	0	0	0.76360	-17.81791	-17.62704



27	-1.13379	-1.13380	-0.72457	0	0	0.76360	-17.81791	-17.62705
28	-0.46459	-0.85035	-0.85035	-0.92918	0	0.75924	-17.92022	-17.72935
29	-1.13380	-1.13379	-0.92918	0	0	0.75493	-18.02252	-17.83166
30	-1.13379	-1.13379	-1.13379	0	0	0.74646	-18.22713	-18.03627



The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant  $k'$  (Eq. (15.1)) is used to determine the ellipsoidal parameter  $c'$  (Eq. (15.2)) of the each  $H_2$ -type-ellipsoidal-MO in terms of the central force of the foci. Then,  $c'$  is substituted into the energy equation (from Eq. (15.11))) which is set equal to  $n_1$  times the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ ,  $-31.63536831 \text{ eV}$ , Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis  $a$  as its only parameter. The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy,  $E_T(H_2MO)$ , is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus  $E_T(AO/HO)$ :

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO) \quad (15.36)$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] + E_T(AO/HO) \\ &= -\frac{n_1 e^2}{8\pi\epsilon_0 c'} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_T(AO/HO) \end{aligned} \quad (15.37)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the group,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and  $E_T(AO/HO)$  is the total energy comprising the difference of the energy  $E(AO/HO)$  of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component  $\Delta E_{H_2MO}(AO/HO)$  due to the AO or HO's charge donation to the MO.

$$E_T(AO/HO) = E(AO/HO) - \Delta E_{H_2MO}(AO/HO) \quad (15.38)$$



As specific examples given in previous sections,  $E_T(AO / HO)$  is one from the group of

$$E_T(AO / HO) = E(O2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV};$$

$$E_T(AO / HO) = E(N2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV};$$

$$E_T(AO / HO) = E(C, 2sp^3) = -14.63489 \text{ eV};$$

$$5 \quad E_T(AO / HO) = E_{Coulomb}(Cl, 3sp^3) = -14.60295 \text{ eV};$$

$$E_T(AO / HO) = E(\text{ionization}; C) + E(\text{ionization}; C^+);$$

$$E_T(AO / HO) = E(C_{ethane}, 2sp^3) = -15.35946 \text{ eV};$$

$$E_T(AO / HO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3);$$

$$E_T(AO / HO) = E(C, 2sp^3) - 2E_T(C = C, 2sp^3) = -14.63489 \text{ eV} - (-2.26758 \text{ eV});$$

$$10 \quad E_T(AO / HO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002 \text{ eV};$$

$$E_T(AO / HO) = E(C, 2sp^3) - 2E_T(C \equiv C, 2sp^3) = -14.63489 \text{ eV} - (-3.13026 \text{ eV});$$

$$E_T(AO / HO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3);$$

$$E_T(AO / HO) = E(C, 2sp^3) - E_T(C = C, 2sp^3) = -14.63489 \text{ eV} - (-1.13379 \text{ eV}), \text{ and}$$

$$E_T(AO / HO) = E(C_{alkane}, 2sp^3) = -15.56407 \text{ eV}.$$

$$15 \quad \text{To solve the bond parameters and energies, } c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}} \quad (\text{Eq.}$$

(15.2)) is substituted into  $E_T(H_2MO)$  to give

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] + E_T(AO / HO) \\ &= -\frac{n_1 e^2}{8\pi\epsilon_0 c'} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_T(AO / HO) \\ &= -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] + E_T(AO / HO) \end{aligned} \quad (15.39)$$

The total energy is set equal to  $E(\text{basis energies})$  which in the most general case is given by



the sum of a first integer  $n_1$  times the total energy of  $H_2$  minus a second integer  $n_2$  times the total energy of  $H$ , minus a third integer  $n_3$  times the valence energy of  $E(AO)$  (e.g.  $E(N) = -14.53414 \text{ eV}$ ) where the first integer can be 1, 2, 3..., and each of the second and third integers can be 0, 1, 2, 3....

$$5 \quad E(\text{basis energies}) = n_1(-31.63536831 \text{ eV}) - n_2(-13.605804 \text{ eV}) - n_3 E(AO) \quad (15.40)$$

In the case that the MO bonds two atoms other than hydrogen,  $E(\text{basis energies})$  is  $n_1$  times the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ ,  $-31.63536831 \text{ eV}$ , Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

$$10 \quad E(\text{basis energies}) = n_1(-31.63536831 \text{ eV}) \quad (15.41)$$

$E_T(H_2MO)$ , is set equal to  $E(\text{basis energies})$ , and the semimajor axis  $a$  is solved.

Thus, the semimajor axis  $a$  is solved from the equation of the form:

$$-\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] + E_T(AO / HO) = E(\text{basis energies}) \quad (15.42)$$

The distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus  $c'$ , the internuclear distance  $2c'$ , and the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO  $b = c$  are solved from the semimajor axis  $a$  using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.39).

The total energy of the MO of the functional group,  $E_T(MO)$ , is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and  $E_T(\text{atom} - \text{atom}, msp^3.AO)$ , the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.39-15.40),  $E_T(MO)$  is

$$E_T(MO) = E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \quad (15.43)$$

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\bar{E}_{osc}$  is the sum of the Doppler,  $\bar{E}_D$ , and average vibrational kinetic energies,  $\bar{E}_{Kvib}$ :



$$\bar{E}_{osc} = n_1 (\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left( E_{hv} \sqrt{\frac{2\bar{E}_K}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (15.44)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $k$  is the spring constant of the equivalent harmonic oscillator, and  $\mu$  is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to  $\bar{E}_D$  is determined by the force  
5 between the central field and the electrons in the transition state. The force and its derivative are given by

$$f(R) = -c_{BO} \frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3} \quad (15.45)$$

and

$$f'(a) = 2c_{BO} \frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3} \quad (15.46)$$

10 such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[ \frac{-3}{a} f(a) - f'(a) \right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO} \frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}{m_e}} \quad (15.47)$$

where  $R$  is the semimajor axis  $a$  or the semiminor axis  $b$  depending on the eccentricity of the bond that is most representative of the oscillation in the transition state,  $c_{BO}$  is the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single  
15 bonds as in the case of functional groups.  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules and 9 for an independent triplet bond.  $C_{1o}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and  $C_{2o}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond.  
20 Typically,  $C_{1o} = C_1$  and  $C_{2o} = C_2$ . The kinetic energy,  $E_K$ , corresponding to  $\bar{E}_D$  is given by Planck's equation for functional groups:

$$\bar{E}_K = \hbar\omega = \hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3 m_e}} \quad (15.48)$$

The Doppler energy of the electrons of the reentrant orbit is



$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{m_e c^2}} = E_{hv} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} \quad (15.49)$$

$\bar{E}_{osc}$  given by the sum of  $\bar{E}_D$  and  $\bar{E}_{Kvib}$  is

$$\bar{E}_{osc} (group) = n_1 (\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left( E_{hv} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} + E_{vib} \right) \quad (15.50)$$

$E_{hv}$  of a group having  $n_1$  bonds is given by  $E_T (MO) / n_1$  such that

$$5 \quad \bar{E}_{osc} = n_1 (\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left( E_T (MO) / n_1 \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (15.51)$$

$E_{T+osc} (Group)$  is given by the sum of  $E_T (MO)$  (Eq. (15.42)) and  $\bar{E}_{osc}$  (Eq. (15.51)):

$$\begin{aligned} E_{T+osc} (Group) &= E_T (MO) + \bar{E}_{osc} \\ &= \left( \left[ -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] \right] \right. \\ &\quad \left. + E_T (AO / HO) + E_T (atom - atom, msp^3 . AO) \right) \\ &\quad \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} \right] + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \\ &= \left( E(basis \text{ energies}) + E_T (atom - atom, msp^3 . AO) \right) \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} \right] + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \end{aligned} \quad (15.52)$$



The total energy of the functional group  $E_T(\text{group})$  is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms,  $E(\text{basis energies})$ , the change in the energy of the AOs or HOs upon forming the bond ( $E_T(\text{atom} - \text{atom}, msp^3.AO)$ ), the energy of oscillation in the transition state, and the  
 5 change in magnetic energy with bond formation,  $E_{mag}$ . From Eq. (15.52), the total energy of the group  $E_T(\text{Group})$  is

$$E_T(\text{Group}) = \left( E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \right) \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_o R^3}}}{m_e c^2}} \right] + n_1 \bar{E}_{Kvib} + E_{mag} \quad (15.53)$$

The change in magnetic energy  $E_{mag}$  which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

$$10 \quad E_{mag} = c_3 \frac{2\pi\mu_o e^2 \hbar^2}{m_e^2 r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \quad (15.54)$$

where  $r^3$  is the radius of the atom that reacts to form the bond and  $c_3$  is the number of electron pairs.

$$E_T(\text{Group}) = \left( E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \right) \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_o R^3}}}{m_e c^2}} \right] + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \quad (15.55)$$

The total bond energy of the group  $E_D(\text{Group})$  is the negative difference of the total energy of  
 15 the group (Eq. (15.55)) and the total energy of the starting species given by the sum of  $c_4 E_{initial}(c_4 AO / HO)$  and  $c_5 E_{initial}(c_5 AO / HO)$ :



$$E_D (Group) = - \left( E(basis\ energies) + E_T (atom - atom, msp^3 . AO) \right) \left[ 1 + \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_o R^3} \frac{2\hbar}{m_e c^2}} \right] + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r_n^3} - (c_4 E_{initial} (AO / HO) + c_5 E_{initial} (c_5 AO / HO)) \quad (15.56)$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the  $C2sp^3$  HO such that

$$E(AO / HO) = -14.63489\ eV \quad (15.57)$$

5 For examples of  $E_{mag}$  from previous sections:

$$E_{mag} (C2sp^3) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{(0.91771a_0)^3} = c_3 0.14803\ eV \quad (15.58)$$

$$E_{mag} (O2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{a_0^3} = c_3 0.11441\ eV \quad (15.59)$$

$$E_{mag} (N2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{(0.93084a_0)^3} = c_3 0.14185\ eV \quad (15.60)$$

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at  $a$ . Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.52-15.59). To meet the equipotential condition for the union of the  $H_2$ -type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

(i) one:

$$c_2 = 1 \quad (15.61)$$

(ii) the ratio that is less than one of  $13.605804\ eV$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243), and the magnitude of the



Coulombic energy of the participating AO or HO of the atom,  $E_{Coulomb}(MO.atom,msp^3)$  given by Eqs. (15.19) and (15.31-15.32). For  $|E_{Coulomb}(MO.atom,msp^3)| > 13.605804 \text{ eV}$  :

$$c_2 = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{A-B \text{ AorBsp}^3}}} = \frac{13.605804 \text{ eV}}{|E_{Coulomb}(MO.atom,msp^3)|} \quad (15.62)$$

For  $|E_{Coulomb}(MO.atom,msp^3)| < 13.605804 \text{ eV}$  :

$$c_2 = \frac{\frac{e^2}{8\pi\epsilon_0 r_{A-B \text{ AorBsp}^3}}}{\frac{e^2}{8\pi\epsilon_0 a_0}} = \frac{|E_{Coulomb}(MO.atom,msp^3)|}{13.605804 \text{ eV}} \quad (15.63)$$

(iii) the ratio that is less than one of 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243), and the magnitude of the valence energy,  $E(valence)$ , of the participating AO or HO of the atom where  $E(valence)$  is the ionization energy or  $E(MO.atom,msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For  $|E(valence)| > 13.605804 \text{ eV}$  :

$$c_2 = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{A-B \text{ AorBsp}^3}}} = \frac{13.605804 \text{ eV}}{|E(valence)|} \quad (15.64)$$

For  $|E(valence)| < 13.605804 \text{ eV}$  :

$$c_2 = \frac{\frac{e^2}{8\pi\epsilon_0 r_{A-B \text{ AorBsp}^3}}}{\frac{e^2}{8\pi\epsilon_0 a_0}} = \frac{|E(valence)|}{13.605804 \text{ eV}} \quad (15.65)$$

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(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom,  $E_{Coulomb}(MO.atom,msp^3)$  given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy,  $E(valence)$ , of the participating AO or HO of a second atom to which the first is energy matched where  $E(valence)$  is the



ionization energy or  $E(MO.atom,msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For

$|E_{Coulomb}(MO.atom,msp^3)| > E(valence)$ :

$$c_2 = \frac{|E(valence)|}{|E_{Coulomb}(MO.atom,msp^3)|} \quad (15.66)$$

For  $|E_{Coulomb}(MO.atom,msp^3)| < E(valence)$ :

$$c_2 = \frac{|E_{Coulomb}(MO.atom,msp^3)|}{|E(valence)|} \quad (15.67)$$

(v) the ratio that is less than one of the magnitude of the valence-level energies,  $E_n(valence)$ , of the AO or HO of the nth participating atom of two that are energy matched where  $E(valence)$  is the ionization energy or  $E(MO.atom,msp^3)$  given by Eqs. (15.20) and (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)} \quad (15.68)$$

(vi) the factor that is the ratio of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.68); alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \quad (15.69)$$

(vii) the factor that is the product of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.69);



alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) \quad (15.70)$$

5 The hybridization factor  $c_2$  corresponds to the force constant  $k$  (Eqs. (11.65) and (13.58)).

In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243), then  $C_2$  corresponding to  $k'$  (Eq. (15.1)) is given by Eqs. (15.62-15.70).

Specific examples of the factors  $c_2$  and  $C_2$  of a  $H_2$ -type ellipsoidal MO of Eq. 10 (15.51) given in following sections are

$$c_2(C2sp^3HO \text{ to } F) = \frac{E(C, 2sp^3)}{E(F)} c_2(C2sp^3HO) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}} (0.91771) = 0.77087;$$

$$C_2(C2sp^3HO \text{ to } Cl) = \frac{E(Cl)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-12.96764 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.81317;$$

$$C_2(C2sp^3HO \text{ to } Br) = \frac{E(Br)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.74081;$$

$$C_2(C2sp^3HO \text{ to } I) = \frac{E(I)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.45126 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.65537;$$

$$15 \quad c_2(C2sp^3HO \text{ to } O) = \frac{E(O)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.85395;$$

$$c_2(H \text{ to } 1^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627;$$

$$c_2(C2sp^3HO \text{ to } N) = \frac{E(N)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.91140;$$

$$c_2(H \text{ to } 2^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383;$$

$$C_2(S3p \text{ to } H) = \frac{E(S, 3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144;$$

$$20 \quad C_2(C2sp^3HO \text{ to } S) = \frac{E(S)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.64965;$$



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$$\begin{aligned}
 c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3HO) &= \frac{E(O)}{E(S)} c_2(C2sp^3HO) \\
 &= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}} (0.91771); \\
 &= 1.20632
 \end{aligned}$$

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045;$$

$$C_2(C2sp^3HO \text{ to } S3sp^3) = \frac{E(S3sp^3)}{E(C,2sp^3)} c_2(S3sp^3) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}} (0.85045) = 0.66951;$$

$$\begin{aligned}
 C_2(S3sp^3 \text{ to } O \text{ to } C2sp^3HO) &= \frac{E(S,3sp^3)}{E(O,2p)} c_2(C2sp^3HO) \\
 &= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}} (0.91771); \\
 &= 0.77641
 \end{aligned}$$

$$\begin{aligned}
 c_2(O \text{ to } N2p \text{ to } C2sp^3HO) &= \frac{E(O)}{E(N)} c_2(C2sp^3HO) \\
 &= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}} (0.91771); \\
 &= 0.85987
 \end{aligned}$$

5

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727;$$

$$C_2(\text{benzene}C2sp^3HO) = c_2(\text{benzene}C2sp^3HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252;$$

$$\begin{aligned}
 c_2(\text{aryl}C2sp^3HO \text{ to } O) &= \frac{E(O)}{E(C,2sp^3)} c_2(\text{aryl}C2sp^3HO) \\
 &= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \quad ; \\
 &= 0.79329
 \end{aligned}$$

$$c_2(H \text{ to aniline } N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171;$$

$$\begin{aligned}
 c_2(\text{aryl}C2sp^3HO \text{ to } N) &= \frac{E(N)}{E(C,2sp^3)} c_2(\text{aryl}C2sp^3HO) \\
 &= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \quad , \\
 &= 0.84665
 \end{aligned}$$

10

and



$$C_2 \left( S3p \text{ to aryl-type } C2sp^3 HO \right) = \frac{E(S, 3p)}{E(C, 2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700.$$

## MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95) wherein the nucleus of a  $B$  atom and the nucleus of a  $A$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO of an  $A-B$  bond.

The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $A$ -atom AO are determined from the polar equation of the ellipse:

$$r = r_0 \frac{1 + e}{1 + e \cos \theta'} \quad (15.71)$$

The radius of the  $A$  shell is  $r_A$ , and the polar radial coordinate of the ellipse and the radius of the  $A$  shell are equal at the point of intersection such that

$$r_A = (a - c') \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a} \cos \theta'} \quad (15.72)$$

The polar angle  $\theta'$  at the intersection point is given by

$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right) \quad (15.73)$$

Then, the angle  $\theta_{AAO}$  the radial vector of the  $A$  AO makes with the internuclear axis is

$$\theta_{AAO} = 180^\circ - \theta' \quad (15.74)$$

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $A$  radial vector obeys the following relationship:

$$r_A \sin \theta_{AAO} = b \sin \theta_{H_2MO} \quad (15.75)$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{r_A \sin \theta_{AAO}}{b} \quad (15.76)$$



The distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \quad (15.77)$$

The distance  $d_{AAO}$  along the internuclear axis from the origin of the  $A$  atom to the point of intersection of the orbitals is given by

$$d_{AAO} = c' - d_{H_2MO} \quad (15.78)$$

## BOND ANGLES

Further consider an  $ACB$  MO comprising a linear combination of  $C-A$ -bond and  $C-B$ -bond MOs where  $C$  is the general central atom. A bond is also possible between the  $A$  and  $B$  atoms of the  $C-A$  and  $C-B$  bonds. Such  $A-B$  bonding would decrease the  $C-A$  and  $C-B$  bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the  $\angle ACB$  bond angle is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal  $A$  and  $B$  atoms is zero. The force constant  $k'$  of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\epsilon_0} \quad (15.79)$$

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal  $A-H$  ( $A$  is  $H$  or other atom) and 1 otherwise and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52). The distance from the origin of the MO to each focus  $c'$  of the  $A-B$  ellipsoidal MO is given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}} \quad (15.80)$$

The internuclear distance is

$$2c' = 2 \sqrt{\frac{aa_0}{2C_1 C_2}} \quad (15.81)$$



The length of the semiminor axis of the prolate spheroidal  $A-B$  MO  $b=c$  is given by Eq. (15.4).

The component energies and the total energy,  $E_T(H_2MO)$ , of the  $A-B$  bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of  $H_2$  except that the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single bonds as in the case of functional groups.  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules. The kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by  $c_1$ , the fraction of the  $H_2$ -type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal  $A-H$  ( $A$  is  $H$  or other atom) and 1 otherwise. The electron energy terms are further multiplied by  $c'_2$ , the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when  $A-B$  comprises atoms other than  $H$ ,  $E_T(atom - atom, msp^3.AO)$ , the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give  $E_T(H_2MO)$ :

$$E_T(H_2MO) = \frac{-e^2}{8\pi\epsilon_0 c'} \left[ c_1 c'_2 \left( 2c_{BO} - c'_{BO} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_T(atom - atom, msp^3.AO) \quad (15.82)$$

The radiation reaction force in the case of the vibration of  $A-B$  in the transition state corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the  $A-B$  MO is given by the sum of  $E_T(H_2MO)$  (Eq. (15.82)) and  $\bar{E}_{osc}$  given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy  $E_T(A-B)$  of the  $A-B$  MO including the Doppler term is



$$E_T(A-B) = \left[ \left( \frac{-e^2}{8\pi\epsilon_0 c'} \left[ c_1 c_2' \left( 2c_{BO} - c'_{BO} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_T(\text{atom} - \text{atom}, msp^3.AO) \right) \right] \quad (15.83)$$

$$\left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{c_{BO} C_{10} C_{20} e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} + \frac{1}{2} \sqrt{\frac{c_{BO} \frac{c_1 c_2' e^2}{8\pi\epsilon_0 a^3} - \frac{c_{BO} e^2}{8\pi\epsilon_0 (a+c')^3}}{\mu}} \right]$$

where  $C_{10}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of the  $A-B$  bond which is 0.75 (Eq. (13.233)) in the case of  $H$  bonding to a central atom and 1 otherwise,  $C_{20}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the  $A-B$  ellipsoidal MO is zero,  $E_T(A-B)$  given by Eq. (15.83) is set equal to zero. Substitution of Eq. (15.81) into Eq. (15.83) gives

$$0 = \left[ \left( \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2' \left( 2c_{BO} - c'_{BO} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] + E_T(\text{atom} - \text{atom}, msp^3.AO) \right) \right] \quad (15.84)$$

$$\left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{c_{BO} C_{10} C_{20} e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} + \frac{1}{2} \sqrt{\frac{c_{BO} \frac{c_1 c_2' e^2}{8\pi\epsilon_0 a^3} - \frac{c_{BO} e^2}{8\pi\epsilon_0 \left( a + \sqrt{\frac{aa_0}{2C_1 C_2}} \right)^3}}{\mu}} \right]$$

The vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by

$$f(a) = -c_{BO} \frac{c_1 c_2' e^2}{4\pi\epsilon_0 a^3} \quad (15.85)$$

and



$$f'(a) = 2c_{BO} \frac{c_1 c'_2 e^2}{4\pi\epsilon_0 a^3} \quad (15.86)$$

The nuclear repulsion force and its derivative are given by

$$f(a+c') = \frac{e^2}{8\pi\epsilon_0 (a+c')^2} \quad (15.87)$$

and

$$f'(a+c') = -\frac{e^2}{4\pi\epsilon_0 (a+c')^3} \quad (15.88)$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[ \frac{-3}{a} f(a) - f'(a) \right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO} \frac{c_1 c'_2 e^2}{4\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^2}}{\mu}} \quad (15.89)$$

Since both terms of  $\bar{E}_{osc} = \bar{E}_D + \bar{E}_{Kvib}$  are small due to the large values of  $a$  and  $c'$ , to very good approximation, a convenient form of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \left[ \left( \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c'_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] + E_r(\text{atom} - \text{atom}, msp^3, AO) \right) \right] \quad (15.90)$$

$$\left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{c_1 e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{\frac{c_1 e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 \left( a + \sqrt{\frac{aa_0}{2C_1 C_2}} \right)^3}}{\mu}} \right]$$

From the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the  $A-B$  MO can be solved. The most convenient way to solve Eq. (15.90) is by the reiterative technique using a computer.

A factor  $c_2$  of a given atom in the determination of  $c'_2$  for calculating the zero of the total  $A-B$  bond energy is typically given by Eqs. (15.62-15.65). In the case of a  $H-H$  terminal bond of an alkyl or alkenyl group,  $c'_2$  is typically the ratio of  $c_2$  of Eq. (15.62) for the  $H-H$  bond which is one and  $c_2$  of the carbon of the corresponding  $C-H$  bond:



$$c'_2 = \frac{1}{c_2(C2sp^3)} = \frac{13.605804 \text{ eV}}{E_{Coulomb}(C-H \text{ } C2sp^3)} \quad (15.91)$$

In the case of the determination of the bond angle of the  $ACH$  MO comprising a linear combination of  $C-A$ -bond and  $C-H$ -bond MOs where  $A$  and  $C$  are general,  $C$  is the central atom, and  $c_2$  for an atom is given by Eqs. (15.62-15.70),  $c'_2$  of the  $A-H$  terminal bond is typically the ratio of  $c_2$  of the  $A$  atom for the  $A-H$  terminal bond and  $c_2$  of the  $C$  atom of the corresponding  $C-H$  bond:

$$c'_2 = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3))} \quad (15.92)$$

In the case of the determination of the bond angle of the  $COH$  MO of an alcohol comprising a linear combination of  $C-O$ -bond and  $O-H$ -bond MOs where  $C$ ,  $O$ , and  $H$  are carbon, oxygen, and hydrogen, respectively,  $c'_2$  of the  $C-H$  terminal bond is typically 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the  $C2sp^3$  HO.

In the determination of the hybridization factor  $c'_2$  of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy,  $E_{Coulomb}(MO.atom,msp^3)$ , or the energy,  $E(MO.atom,msp^3)$ , the radius  $r_{A-B \text{ } AorBsp^3}$  of the  $A$  or  $B$  AO or HO of the heteroatom of the  $A-B$  terminal bond MO such as the  $C2sp^3$  HO of a terminal  $C-C$  bond is calculated using Eq. (15.32) by considering  $\sum E_{T_{mol}}(MO,2sp^3)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy  $E_{Coulomb}(MO.atom,msp^3)$  of the outer electron of the  $atom \text{ } msp^3$  shell is given by Eq. (15.19).

In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(magnetic)$  (Eq. (15.15)) at the initial radius  $r$  of the AO electron. Then, the energy  $E(MO.atom,msp^3)$  of the outer electron of the  $atom \text{ } msp^3$  shell is given by the sum of  $E_{Coulomb}(MO.atom,msp^3)$  and  $E(magnetic)$  (Eq. (15.20)).

In the specific case of the terminal bonding of two carbon atoms, the  $c_2$  factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy  $E_{Coulomb}(C-C \text{ } C2sp^3)$  of the outer electron of the  $C2sp^3$  shell given by Eq. (15.19) with the



radius  $r_{C-C\ C2sp^3}$  of each  $C2sp^3$  HO of the terminal  $C-C$  bond calculated using Eq. (15.32)

by considering  $\sum E_{T_{mol}}(MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy,  $0.92918\ eV$  (Eq. (14.513)), corresponding to the terminal  $C-C$  bond.

5 The corresponding  $E_T(atom - atom, msp^3.AO)$  in Eq. (15.90) is  $E_T(C - C\ C2sp^3) = -1.85836\ eV$ .

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus,  $c'_2$  is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

$$10 \quad c'_2 = \frac{1}{2} (c'_2(atom\ 1) + c'_2(atom\ 2)) \quad (15.93)$$

In the exemplary cases of  $C-C$ ,  $O-O$ , and  $N-N$  where  $C$  is carbon:

$$\begin{aligned} c'_2 &= \frac{1}{2} \left( \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{A-A_1 AO/HO}}} + \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{A-A_2 AO/HO}}} \right) \\ &= \frac{1}{2} \left( \frac{13.605804\ eV}{E_{Coulomb}(A - A_1 AO / HO)} + \frac{13.605804\ eV}{E_{Coulomb}(A - A_2 AO / HO)} \right) \end{aligned} \quad (15.94)$$

In the exemplary cases of  $C-N$ ,  $C-O$ , and  $C-S$ ,

$$c'_2 = \frac{1}{2} \left( \frac{13.605804\ eV}{E_{Coulomb}(C - B\ C2sp^3)} + c_2(C\ to\ B) \right) \quad (15.95)$$

15 where  $C$  is carbon and  $c_2(C\ to\ B)$  is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom  $B$  to that of the atom  $C$  in the group. For these cases, the corresponding  $E_T(atom - atom, msp^3.AO)$  term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

$$\begin{aligned} 20 \quad E_T(C - O\ C2sp^3.O2p) &= -1.44915\ eV; & E_T(C - O\ C2sp^3.O2p) &= -1.65376\ eV; \\ E_T(C - N\ C2sp^3.N2p) &= -1.44915\ eV; & E_T(C - S\ C2sp^3.S2p) &= -0.72457\ eV; \\ E_T(O - O\ O2p.O2p) &= -1.44915\ eV; & E_T(O - O\ O2p.O2p) &= -1.65376\ eV; \end{aligned}$$



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$$\begin{aligned}
E_T(N-N N2p.N2p) &= -1.44915 \text{ eV}; & E_T(N-O N2p.O2p) &= -1.44915 \text{ eV}; \\
E_T(F-F F2p.F2p) &= -1.44915 \text{ eV}; & E_T(Cl-Cl Cl3p.Cl3p) &= -0.92918 \text{ eV}; \\
E_T(Br-Br Br4p.Br4p) &= -0.92918 \text{ eV}; & E_T(I-I I5p.I5p) &= -0.36229 \text{ eV}; \\
E_T(C-F C2sp^3.F2p) &= -1.85836 \text{ eV}; & E_T(C-Cl C2sp^3.Cl3p) &= -0.92918 \text{ eV}; \\
5 \quad E_T(C-Br C2sp^3.Br4p) &= -0.72457 \text{ eV}; & E_T(C-I C2sp^3.I5p) &= -0.36228 \text{ eV}, \text{ and} \\
E_T(O-Cl O2p.Cl3p) &= -0.92918 \text{ eV}.
\end{aligned}$$

In the case that the terminal bond is  $X-X$  where  $X$  is a halogen atom,  $c_1$  is one, and  $c'_2$  is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where  $E_{Coulomb}(MO.atom,msp^3)$  is determined using Eq. (15.32) and  $E_{Coulomb}(MO.atom,msp^3) = 13.605804 \text{ eV}$  for  $X = I$ . The factor  $C_1$  of Eq. (15.90) is one for all halogen atoms. The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that  $13.605804 \text{ eV}$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). For each of the other halogens,  $Cl$ ,  $Br$ , and  $I$ ,  $C_2$  is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with  $c_2(1)$  being that of the halogen given by Eq. (15.68) that matches the valence energy of  $X$  ( $E_1(valence)$ ) to that of the  $C2sp^3$  HO ( $E_2(valence) = -14.63489 \text{ eV}$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)).  $E_T(atom-atom,msp^3.AO)$  of Eq. (15.90) is the maximum for the participating atoms which is  $-1.44915 \text{ eV}$ ,  $-0.92918 \text{ eV}$ ,  $-0.92918 \text{ eV}$ , and  $-0.33582 \text{ eV}$  for  $F$ ,  $Cl$ ,  $Br$ , and  $I$ , respectively.

Consider the case that the terminal bond is  $C-X$  where  $C$  is a carbon atom and  $X$  is a halogen atom. The factors  $c_1$  and  $C_1$  of Eq. (15.90) are one for all halogen atoms. For  $X = F$ ,  $c'_2$  is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and  $F$  atoms where  $c_2$  for carbon is given by Eq. (15.62) and  $c_2$  for fluorine matched to carbon is given by Eq. (15.70) with  $c_2(1)$  for the fluorine atom given by Eq. (15.68) that matches the valence energy of  $F$  ( $E_1(valence) = -17.42282 \text{ eV}$ ) to that of the  $C2sp^3$  HO



( $E_2(\text{valence}) = -14.63489 \text{ eV}$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)). The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that  $13.605804 \text{ eV}$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). For each of the other halogens,  $Cl$ ,  $Br$ , and  $I$ ,  $c'_2$  is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom.  $C_2$  of the terminal-atom bond matches that used to determine the energies of the corresponding  $C-X$ -bond MO. Then,  $C_2$  is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with  $c_2(1)$  for the halogen atom given by Eq. (15.68) that matches the valence energy of  $X$  ( $E_1(\text{valence})$ ) to that of the  $C2sp^3$  HO ( $E_2(\text{valence}) = -14.63489 \text{ eV}$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)).  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of Eq. (15.90) is the maximum for the participating atoms which is  $-1.85836 \text{ eV}$ ,  $-0.92918 \text{ eV}$ ,  $-0.72457 \text{ eV}$ , and  $-0.33582 \text{ eV}$  for  $F$ ,  $Cl$ ,  $Br$ , and  $I$ , respectively.

Consider the case that the terminal bond is  $H-X$  corresponding to the angle of the atoms  $H CX$  where  $C$  is a carbon atom and  $X$  is a halogen atom. The factors  $c_1$  and  $C_1$  of Eq. (15.90) are 0.75 for all halogen atoms. For  $X = F$ ,  $c'_2$  is given by Eq. (15.69) with  $c_2$  of the participating carbon and  $F$  atoms given by Eq. (15.62) and Eq. (15.65), respectively. The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that  $13.605804 \text{ eV}$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). For each of the other halogens,  $Cl$ ,  $Br$ , and  $I$ ,  $c'_2$  is also given by Eq. (15.69) with  $c_2$  of the participating carbon given by Eq. (15.62) and  $c_2$  of the participating  $X$  atom given by  $c_2 = 0.91771$  (Eq. (13.430)) since the  $X$  atom is energy matched to the  $C2sp^3$  HO. In these cases,  $C_2$  is given by Eq. (15.65) for the corresponding atom  $X$  where  $C_2$  matches the energy of the atom  $X$  to that of  $H$ .

Using the distance between the two atoms  $A$  and  $B$  of the general molecular group  $ACB$  when the total energy of the corresponding  $A-B$  MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1s_2\cosine\theta = s_3^2 \quad (15.96)$$



With  $s_1 = 2c'_{C-A}$ , the internuclear distance of the  $C-A$  bond,  $s_2 = 2c'_{C-B}$ , the internuclear distance of each  $C-B$  bond, and  $s_3 = 2c'_{A-B}$ , the internuclear distance of the two terminal atoms, the bond angle  $\theta_{ACB}$  between the  $C-A$  and  $C-B$  bonds is given by

$$(2c'_{C-A})^2 + (2c'_{C-B})^2 - 2(2c'_{C-A})(2c'_{C-B})\cos\theta = (2c'_{A-B})^2 \quad (15.97)$$

$$5 \quad \theta_{ACB} = \cos^{-1} \left( \frac{(2c'_{C-A})^2 + (2c'_{C-B})^2 - (2c'_{A-B})^2}{2(2c'_{C-A})(2c'_{C-B})} \right) \quad (15.98)$$

Consider the exemplary structure  $C_b C_a (O_a) O_b$  wherein  $C_a$  is bound to  $C_b$ ,  $O_a$ , and  $O_b$ . In the general case that the three bonds are coplanar and two of the angles are known, say  $\theta_1$  and  $\theta_2$ , then the third  $\theta_3$  can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \quad (15.99)$$

10 In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say  $\theta_1$ , then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2} \quad (15.100)$$

## ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES

### 15 TRIANGLE

In the general case where the group comprises three  $A-B$  bonds having  $B$  as the central atom at the apex of a pyramidal structure formed by the three bonds with the  $A$  atoms at the base in the xy-plane. The  $C_{3v}$  axis centered on  $B$  is defined as the vertical or z-axis, and any two  $A-B$  bonds form an isosceles triangle. Then, the angle of the bonds and the distances  
20 from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance  $d_{origin-B}$  from the origin to the nucleus of a terminal  $B$  atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60^\circ} \quad (15.101)$$

the height along the z-axis from the origin to the  $A$  nucleus  $d_{height}$  is given by

$$25 \quad d_{height} = \sqrt{(2c'_{A-B})^2 - (d_{origin-B})^2}, \text{ and} \quad (15.102)$$



the angle  $\theta_v$  of each  $A-B$  bond from the z-axis is given by

$$\theta_v = \tan^{-1} \left( \frac{d_{\text{origin}-B}}{d_{\text{height}}} \right) \quad (15.103)$$

Consider the case where the central atom  $B$  is further bound to a fourth atom  $C$  and the  $B-C$  bond is along the z-axis. Then, the bond  $\theta_{\angle ABC}$  given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_v \quad (15.104)$$

## DIHEDRAL ANGLE

Consider the plane defined by a general  $ACA$  MO comprising a linear combination of two  $C-A$ -bond MOs where  $C$  is the central atom. The dihedral angle  $\theta_{\angle BCI/ACA}$  between the  $ACA$ -plane and a line defined by a third bond with  $C$ , specifically that corresponding to a  $C-B$ -bond MO, is calculated from the bond angle  $\theta_{\angle ACA}$  and the distances between the  $A$ ,  $B$ , and  $C$  atoms. The distance  $d_1$  along the bisector of  $\theta_{\angle ACA}$  from  $C$  to the internuclear-distance line between  $A$  and  $A$ ,  $2c'_{A-A}$ , is given by

$$d_1 = 2c'_{C-A} \cos \frac{\theta_{\angle ACA}}{2} \quad (15.105)$$

where  $2c'_{C-A}$  is the internuclear distance between  $A$  and  $C$ . The atoms  $A$ ,  $A$ , and  $B$  define the base of a pyramid. Then, the pyramidal angle  $\theta_{\angle ABA}$  can be solved from the internuclear distances between  $A$  and  $A$ ,  $2c'_{A-A}$ , and between  $A$  and  $B$ ,  $2c'_{A-B}$ , using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1} \left( \frac{(2c'_{A-B})^2 + (2c'_{A-B})^2 - (2c'_{A-A})^2}{2(2c'_{A-B})(2c'_{A-B})} \right) \quad (15.106)$$

Then, the distance  $d_2$  along the bisector of  $\theta_{\angle ABA}$  from  $B$  to the internuclear-distance line  $2c'_{A-A}$ , is given by

$$d_2 = 2c'_{A-B} \cos \frac{\theta_{\angle ABA}}{2} \quad (15.107)$$

The lengths  $d_1$ ,  $d_2$ , and  $2c'_{C-B}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between  $B$  and  $C$ ,  $2c'_{C-B}$ , is the dihedral angle  $\theta_{\angle BCI/ACA}$  that can be solved using the law of cosines (Eq. (15.98)):



$$\theta_{\angle BC/ACA} = \cos^{-1} \left( \frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{B-C})} \right) \quad (15.108)$$

## SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies were linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitals solutions bridged by molecular orbitals comprised of the  $H_2$ -type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy  $E_{mag}$  (e.g. given by Eq. (15.58)) for a  $C2sp^3$  HO and Eq.(15.59) for an  $O2p$  AO) was subtracted for each set of unpaired electrons created by bond breakage.

The bond energy is not equal to the component energy of each bond as it exists in the molecule; although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will effect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and  $E(C,2sp^3) = -14.63489 \text{ eV}$  (Eq. (13.428)). The intercept angles are determined from Eqs.



(15.71-15.78) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the  
5 corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the  
10 resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry  
15 reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the  
20 drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation  
25 dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.



## AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple  $H_2$ -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule ( $C_6H_6$ ) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

$C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a  $C-H$  bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a  $C=C$  bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule ( $CH_2CH_2$ ) section. The radius  $r_{ethylene 2sp^3}$  ( $0.85252a_0$ ) of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  ( $-15.95955 eV$ ) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  ( $-15.76868 eV$ ) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.246).  $E_T(C=C, 2sp^3)$  ( $-1.13380 eV$ ) (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the  $C=C$ -bond MO is given by the difference between  $E(C_{ethylene}, 2sp^3)$  and  $E(C, 2sp^3)$ .  $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each  $2sp^3$  HO of each carbon atom initially has four unpaired electrons. Thus, the 6  $H$  atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon atoms contribute twenty-four electrons to form six  $C-H$  bonds and six  $C=C$  bonds. Each  $C-H$  bond has two paired electrons with one donated from the  $H$  AO and the other from the  $C2sp^3$  HO. Each  $C=C$  bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each  $C-H$  and each  $C=C$  bond comprises a linear combination of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of  $C=C$ -bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$\left[ \begin{array}{l} 3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3 \overset{4e}{(C=C)} - \text{ethylene-type-bond MO} \\ \rightarrow 6 \overset{3e}{(C=C)} - \text{bond MO of benzene} \end{array} \right] \quad (15.142)$$



The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the  $C=C$ -bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond  $C=C$ -bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the  $C=C$ -bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each  $C=C$ -bond gives rise to the  $C_{benzene}2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C_{benzene}, 2sp^3)$  given by Eq. (14.245). To meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $C_2$  of Eq. (15.42) for the

aromatic  $C=C$ -bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  $E_{Coulomb}(C_{benzene}, 2sp^3)$  (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  (Eq. (1.243)):

$$C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252 \quad (15.143)$$

The energies of each  $C=C$  bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of

benzene. Ethylene serves as a basis element for the  $C=C$  bonding of benzene wherein each of the six  $C=C$  bonds of benzene comprises  $(0.75)(4) = 3$  electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the  $C=C$  bonds of benzene,  $E_T(C_6H_6, C=C)$ , is given by  $(6)(0.75)$  times  $E_{T+osc}(C=C)$  (Eq. (14.492)), the total energy of

the  $C=C$ -bond MO of benzene including the Doppler term, minus eighteen times  $E(C, 2sp^3)$

(Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each  $C$  that forms the  $C=C$  bonds of bond order two. Thus, the total energy of the six  $C=C$  bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned} E_T\left(C_6H_6, C=C\right) &= (6)(0.75)E_{T+osc}(C=C) - (6)(3)E(C, 2sp^3) \\ &= (6)(0.75)(-66.05796 \text{ eV}) - 18(-14.63489 \text{ eV}) \\ &= -297.26081 \text{ eV} - (-263.42798 \text{ eV}) \\ &= -33.83284 \text{ eV} \end{aligned} \quad (15.144)$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.  $E_{hv}$  of an aromatic bond is given by  $E_T(H_2)$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_2$ -type MO such that

$$\bar{E}_{osc} = n_1(\bar{E}_D + \bar{E}_{Kvib}) = n_1\left[-31.63536831 \text{ eV} \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right] \quad (15.145)$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule ( $C_6H_6$ ) section modifies Eqs. (15.52-15.56). Multiplication of



the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_T(\text{Group}) = f_1 \left[ \begin{aligned} & E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \\ & -31.63536831 \text{ eV} \sqrt{\frac{2\hbar \sqrt{\frac{C_{10} C_{20} e^2}{4\pi\epsilon_0 R^3}}}{m_e} + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3}} \end{aligned} \right] \quad (15.146)$$

- 5 The total bond energy of the aromatic group  $E_D(\text{Group})$  is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of  $c_4 E_{\text{initial}}(c_4 AO / HO)$  and  $c_5 E_{\text{initial}}(c_5 AO / HO)$ :

$$E_D(\text{Group}) = - \left[ \begin{aligned} & f_1 \left[ \begin{aligned} & E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \\ & -31.63536831 \text{ eV} \sqrt{\frac{2\hbar \sqrt{\frac{C_{10} C_{20} e^2}{4\pi\epsilon_0 R^3}}}{m_e} + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3}} \end{aligned} \right] \\ & - (c_4 E_{\text{initial}}(AO / HO) + c_5 E_{\text{initial}}(c_5 AO / HO)) \end{aligned} \right] \quad (15.147)$$

10 Since there are three electrons per aromatic bond,  $c_4$  is three times the number of aromatic bonds.

- Benzene can also be considered as comprising chemical bonds between six  $CH$  radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of  $CH$  is given in the Hydrogen Carbide ( $CH$ ) section. Those of the benzene are given in the Benzene Molecule ( $C_6H_6$ ) section. The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that  $E_T(C = C, 2sp^3) = -1.13379 \text{ eV}$  (Eq. (14.247)) is subtracted from  $E_T(CH)$  of Eq. (13.495) to match the energy of each  $C-H$ -bond MO to the decrease in the energy of the corresponding  $C2sp^3 HO$ . In the corresponding generalization of the aromatic  $CH$  group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with  $E_T(\text{atom} - \text{atom}, msp^3.AO) = -1.13379 \text{ eV}$ .

- The total energy of the benzene  $C-H$ -bond MO,  $E_{T_{\text{benzene}}}(C-H)$ , given by Eq. (14.467) is the sum of  $0.5E_T(C = C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell per single bond due to the decrease in radius with the formation of the corresponding  $C=C$ -bond MO (Eq. (14.247)), and  $E_{T_{\text{benzene}}}(CH)$ , the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic  $CH$  group, the energy parameters are determined using Eqs. (15.146-15.147) with  $f_1 = 1$  and  $E_T(\text{atom} - \text{atom}, msp^3.AO) = \frac{-1.13379 \text{ eV}}{2}$ . Thus, the energy



contribution to the single aromatic  $CH$  bond is one half that of the  $C=C$  double bond contribution. This matches the energies of the  $CH$  and  $C=C$  aromatic groups, conserves the electron number with the equivalent charge density as that of  $s=1$  in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic  $C=C$  bonds to give  $CH$  groups creates unpaired electrons in these fragments that corresponds to  $c_3=1$  in Eq. (15.56) with  $E_{mag}$  given by Eq. (15.58).

Each of the  $C-H$  bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each  $C-H$  bond,  $-E_{D_{benzene}}(^{12}CH)$  (Eq. (14.477)), the total energy of the twelve electrons of the six  $C-H$  bonds of benzene,  $E_T(C_6H_6, C-H)$ , given by Eq. (14.494) is

$$E_T(C_6H_6, C-H) = (6)(-E_{D_{benzene}}(^{12}CH)) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV} \quad (15.148)$$

The total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , given by Eq. (14.495) is the negative sum of  $E_T(C_6H_6, C=C)$  (Eq. (14.493)) and  $E_T(C_6H_6, C-H)$  (Eq. (14.494)):

$$\begin{aligned} E_D(C_6H_6) &= -\left(E_T(C_6H_6, C=C) + E_T(C_6H_6, C-H)\right) \\ &= -((-33.83284 \text{ eV}) + (-23.42724 \text{ eV})) \\ &= 57.2601 \text{ eV} \end{aligned} \quad (15.149)$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule ( $C_6H_6$ ) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each  $E_{D(Group)}$  of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

Functional Group	Group Symbol
CC (aromatic bond)	$C=C$
CH (aromatic)	$CH$ (i)



Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and experimental values [1].

Parameter	$^{3e}$ $C=C$ Group	$CH$ Group
$a (a_0)$	1.47348	1.60061
$c' (a_0)$	1.31468	1.03299
Bond Length $2c' (\square)$	1.39140	1.09327
Exp. Bond Length ( $\square$ )	1.399 (benzene)	1.101 (benzene)
$b, c (a_0)$	0.66540	1.22265
$e$	0.89223	0.64537

5 Table 15.216. The energy parameters (eV) of functional groups of aromatics and heterocyclics.

Parameters	$^{3e}$ $C=C$ Group	$CH$ Group
$f_1$	0.75	1
$n_1$	2	1
$n_2$	0	0
$n_3$	0	0
$C_1$	0.5	0.75
$C_2$	0.85252	1
$c_1$	1	1
$c_2$	0.85252	0.91771
$c_3$	0	1
$c_4$	3	1
$c_5$	0	1
$C_{1o}$	0.5	0.75
$C_{2o}$	0.85252	1
$V_e (eV)$	-101.12679	-37.10024
$V_p (eV)$	20.69825	13.17125
$T (eV)$	34.31559	11.58941
$V_m (eV)$	-17.15779	-5.79470
$E_{(AO/HO)} (eV)$	0	-14.63489
$\Delta E_{H_2MO (AO/HO)} (eV)$	0	-1.13379



$E_T (AO/HO) (eV)$	0	-13.50110
$E_T (H_2MO) (eV)$	-63.27075	-31.63539
$E_T (atom - atom, msp^3 AO) (eV)$	-2.26759	-0.56690
$E_T (MO) (eV)$	-65.53833	-32.20226
$\omega (10^{15} rad / s)$	49.7272	26.4826
$E_K (eV)$	32.73133	17.43132
$\bar{E}_D (eV)$	-0.35806	-0.26130
$\bar{E}_{Kvib} (eV)$	0.19649 [49]	0.35532 Eq. (13.458)
$\bar{E}_{osc} (eV)$	-0.25982	-0.08364
$E_{mag} (eV)$	0.14803	0.14803
$E_T (Group) (eV)$	-49.54347	-32.28590
$E_{initial} (e_4 AO/HO) (eV)$	-14.63489	-14.63489
$E_{initial} (e_5 AO/HO) (eV)$	0	-13.59844
$E_D (Group) (eV)$	5.63881	3.90454



Table 15.215. The MO to HO intercept geometrical bond parameters of benzene.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}^3 \text{AO})$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{\text{initial}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )
$C-H$ (CH)	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597
${}^{3e}C=HC_a=C$	$C_a$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597

Bond	$E_{\text{Conlamb}}$ ( $C2sp^3$ )(eV) Final	$E(C2sp^3)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H$ (CH)	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
${}^{3e}C=HC_a=C$	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Formula	Name	${}^{3e}C=C$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_6$	Benzene	6	6	57.26008	57.26340	0.00006



Table 15.218. The bond angle parameters of benzene and experimental values [1].  $E_r$  is  $E_r(atom - atom, msp^3 AO)$ .

Atoms of Angle	$2c'$ Bond 1 ( $a_0$ )	$2c'$ Bond 2 ( $a_0$ )	$2c'$ Terminal Atoms ( $a_0$ )	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1
$\angle CCH$ (aromatic)											

Atoms of Angle	$c_1$	$c'_2$	$E_r$ (eV)	$\theta_v$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle CCC$ (aromatic)	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)					120.19		119.91	120 [50-52] (benzene)



Table 1.1. The calculated and experimental total bond energies of n-alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>8</sub>	Propane	41.46896	41.434	-0.00085
C <sub>4</sub> H <sub>10</sub>	Butane	53.62666	53.61	-0.00036
C <sub>5</sub> H <sub>12</sub>	Pentane	65.78436	65.77	-0.00017
C <sub>6</sub> H <sub>14</sub>	Hexane	77.94206	77.93	-0.00019
C <sub>7</sub> H <sub>16</sub>	Heptane	90.09976	90.09	-0.00013
C <sub>8</sub> H <sub>18</sub>	Octane	102.25746	102.25	-0.00006
C <sub>9</sub> H <sub>20</sub>	Nonane	114.41516	114.40	-0.00012
C <sub>10</sub> H <sub>22</sub>	Decane	126.57286	126.57	-0.00003
C <sub>11</sub> H <sub>24</sub>	Undecane	138.73056	138.736	0.00004
C <sub>12</sub> H <sub>26</sub>	Dodecane	150.88826	150.88	-0.00008
C <sub>18</sub> H <sub>38</sub>	Octadecane	223.83446	223.85	0.00008

Table 1.2. The calculated and experimental total bond energies of branched alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>4</sub> H <sub>10</sub>	Isobutane	53.69922	53.695	-0.00007
C <sub>5</sub> H <sub>12</sub>	Isopentane	65.85692	65.843	-0.00021
C <sub>5</sub> H <sub>12</sub>	Neopentane	65.86336	65.992	0.00195
C <sub>6</sub> H <sub>14</sub>	2-Methylpentane	78.01462	78.007	-0.00010
C <sub>6</sub> H <sub>14</sub>	3-Methylpentane	78.01462	77.979	-0.00046
C <sub>6</sub> H <sub>14</sub>	2,2-Dimethylbutane	78.02106	78.124	0.00132
C <sub>6</sub> H <sub>14</sub>	2,3-Dimethylbutane	77.99581	78.043	0.00061
C <sub>7</sub> H <sub>16</sub>	2-Methylhexane	90.17232	90.160	-0.00014
C <sub>7</sub> H <sub>16</sub>	3-Methylhexane	90.17232	90.127	-0.00051
C <sub>7</sub> H <sub>16</sub>	3-Ethylpentane	90.17232	90.108	-0.00072
C <sub>7</sub> H <sub>16</sub>	2,2-Dimethylpentane	90.17876	90.276	0.00107
C <sub>7</sub> H <sub>16</sub>	2,2,3-Trimethylbutane	90.22301	90.262	0.00044
C <sub>7</sub> H <sub>16</sub>	2,4-Dimethylpentane	90.24488	90.233	-0.00013
C <sub>7</sub> H <sub>16</sub>	3,3-Dimethylpentane	90.17876	90.227	0.00054
C <sub>8</sub> H <sub>18</sub>	2-Methylheptane	102.33002	102.322	-0.00008
C <sub>8</sub> H <sub>18</sub>	3-Methylheptane	102.33002	102.293	-0.00036
C <sub>8</sub> H <sub>18</sub>	4-Methylheptane	102.33002	102.286	-0.00043
C <sub>8</sub> H <sub>18</sub>	3-Ethylhexane	102.30169	102.274	-0.00027
C <sub>8</sub> H <sub>18</sub>	2,2-Dimethylhexane	102.33646	102.417	0.00079
C <sub>8</sub> H <sub>18</sub>	2,3-Dimethylhexane	102.31121	102.306	-0.00005
C <sub>8</sub> H <sub>18</sub>	2,4-Dimethylhexane	102.40258	102.362	-0.00040
C <sub>8</sub> H <sub>18</sub>	2,5-Dimethylhexane	102.40258	102.396	-0.00006
C <sub>8</sub> H <sub>18</sub>	3,3-Dimethylhexane	102.33646	102.369	0.00032
C <sub>8</sub> H <sub>18</sub>	3,4-Dimethylhexane	102.31121	102.296	-0.00015
C <sub>8</sub> H <sub>18</sub>	3-Ethyl-2-methylpentane	102.31121	102.277	-0.00033
C <sub>8</sub> H <sub>18</sub>	3-Ethyl-3-methylpentane	102.33646	102.317	-0.00019
C <sub>8</sub> H <sub>18</sub>	2,2,3-Trimethylpentane	102.38071	102.370	-0.00010
C <sub>8</sub> H <sub>18</sub>	2,2,4-Trimethylpentane	102.40902	102.412	0.00003
C <sub>8</sub> H <sub>18</sub>	2,3,3-Trimethylpentane	102.38071	102.332	-0.00048
C <sub>8</sub> H <sub>18</sub>	2,3,4-Trimethylpentane	102.29240	102.342	0.00049
C <sub>8</sub> H <sub>18</sub>	2,2,3,3-Tetramethylbutane	102.41632	102.433	0.00016
C <sub>9</sub> H <sub>20</sub>	2,3,5-Trimethylhexane	114.54147	114.551	0.00008
C <sub>9</sub> H <sub>20</sub>	3,3-Diethylpentane	114.49416	114.455	-0.00034
C <sub>9</sub> H <sub>20</sub>	2,2,3,3-Tetramethylpentane	114.57402	114.494	-0.00070
C <sub>9</sub> H <sub>20</sub>	2,2,3,4-Tetramethylpentane	114.51960	114.492	-0.00024



Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>9</sub> H <sub>20</sub>	2,2,4,4-Tetramethylpentane	114.57316	114.541	-0.00028
C <sub>9</sub> H <sub>20</sub>	2,3,3,4-Tetramethylpentane	114.58266	114.484	-0.00086
C <sub>10</sub> H <sub>22</sub>	2-Methylnonane	126.64542	126.680	0.00027
C <sub>10</sub> H <sub>22</sub>	5-Methylnonane	126.64542	126.663	0.00014

Table 1.3. The calculated and experimental total bond energies of alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>6</sub>	Propene	35.56033	35.63207	0.00201
C <sub>4</sub> H <sub>8</sub>	1-Butene	47.71803	47.78477	0.00140
C <sub>4</sub> H <sub>8</sub>	trans-2-Butene	47.93116	47.90395	-0.00057
C <sub>4</sub> H <sub>8</sub>	Isobutene	47.90314	47.96096	0.00121
C <sub>5</sub> H <sub>10</sub>	1-Pentene	59.87573	59.95094	0.00125
C <sub>5</sub> H <sub>10</sub>	trans-2-Pentene	60.08886	60.06287	-0.00043
C <sub>5</sub> H <sub>10</sub>	2-Methyl-1-butene	60.06084	60.09707	0.00060
C <sub>5</sub> H <sub>10</sub>	2-Methyl-2-butene	60.21433	60.16444	-0.00083
C <sub>5</sub> H <sub>10</sub>	3-Methyl-1-butene	59.97662	60.01727	0.00068
C <sub>6</sub> H <sub>12</sub>	1-Hexene	72.03343	72.12954	0.00133
C <sub>6</sub> H <sub>12</sub>	trans-2-Hexene	72.24656	72.23733	-0.00013
C <sub>6</sub> H <sub>12</sub>	trans-3-Hexene	72.24656	72.24251	-0.00006
C <sub>6</sub> H <sub>12</sub>	2-Methyl-1-pentene	72.21854	72.29433	0.00105
C <sub>6</sub> H <sub>12</sub>	2-Methyl-2-pentene	72.37203	72.37206	0.00000
C <sub>6</sub> H <sub>12</sub>	3-Methyl-1-pentene	72.13432	72.19173	0.00080
C <sub>6</sub> H <sub>12</sub>	4-Methyl-1-pentene	72.10599	72.21038	0.00145
C <sub>6</sub> H <sub>12</sub>	3-Methyl-trans-2-pentene	72.37203	72.33268	-0.00054
C <sub>6</sub> H <sub>12</sub>	4-Methyl-trans-2-pentene	72.34745	72.31610	-0.00043
C <sub>6</sub> H <sub>12</sub>	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C <sub>6</sub> H <sub>12</sub>	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C <sub>6</sub> H <sub>12</sub>	3,3-Dimethyl-1-butene	72.31796	72.30366	-0.00020
C <sub>6</sub> H <sub>12</sub>	2,3-Dimethyl-2-butene	72.49750	72.38450	-0.00156
C <sub>7</sub> H <sub>14</sub>	1-Heptene	84.19113	84.27084	0.00095
C <sub>7</sub> H <sub>14</sub>	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C <sub>7</sub> H <sub>14</sub>	trans-3-Methyl-3-hexene	84.52973	84.42112	-0.00129
C <sub>7</sub> H <sub>14</sub>	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C <sub>7</sub> H <sub>14</sub>	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C <sub>7</sub> H <sub>14</sub>	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102
C <sub>7</sub> H <sub>14</sub>	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C <sub>7</sub> H <sub>14</sub>	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C <sub>7</sub> H <sub>14</sub>	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C <sub>8</sub> H <sub>16</sub>	1-Octene	96.34883	96.41421	0.00068
C <sub>8</sub> H <sub>16</sub>	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C <sub>8</sub> H <sub>16</sub>	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C <sub>8</sub> H <sub>16</sub>	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C <sub>8</sub> H <sub>16</sub>	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
C <sub>10</sub> H <sub>20</sub>	1-Decene	120.66423	120.74240	0.00065
C <sub>12</sub> H <sub>24</sub>	1-Dodecene	144.97963	145.07163	0.00063
C <sub>16</sub> H <sub>32</sub>	1-Hexadecene	193.61043	193.71766	0.00055



Table 1.4. The calculated and experimental total bond energies of alkynes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>4</sub>	Propyne	29.42932	29.40432	-0.00085
C <sub>4</sub> H <sub>6</sub>	1-Butyne	41.58702	41.55495	-0.00077
C <sub>4</sub> H <sub>6</sub>	2-Butyne	41.72765	41.75705	0.00070
C <sub>9</sub> H <sub>16</sub>	1-Nonyne	102.37552	102.35367	-0.00021

Table 1.5. The calculated and experimental total bond energies of alkyl fluorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF <sub>4</sub>	Tetrafluoromethane	21.07992	21.016	-0.00303
CHF <sub>3</sub>	Trifluoromethane	19.28398	19.362	0.00405
CH <sub>2</sub> F <sub>2</sub>	Difluoromethane	18.22209	18.280	0.00314
C <sub>3</sub> H <sub>7</sub> F	1-Fluoropropane	41.86745	41.885	0.00041
C <sub>3</sub> H <sub>7</sub> F	2-Fluoropropane	41.96834	41.963	-0.00012

Table 1.6. The calculated and experimental total bond energies of alkyl chlorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CCl <sub>4</sub>	Tetrachloromethane	13.43181	13.448	0.00123
CHCl <sub>3</sub>	Trichloromethane	14.49146	14.523	0.00217
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane	15.37248	15.450	0.00499
CH <sub>3</sub> Cl	Chloromethane	16.26302	16.312	0.00299
C <sub>2</sub> H <sub>5</sub> Cl	Chloroethane	28.61064	28.571	-0.00138
C <sub>3</sub> H <sub>7</sub> Cl	1-Chloropropane	40.76834	40.723	-0.00112
C <sub>3</sub> H <sub>7</sub> Cl	2-Chloropropane	40.86923	40.858	-0.00028
C <sub>4</sub> H <sub>9</sub> Cl	1-Chlorobutane	52.92604	52.903	-0.00044
C <sub>4</sub> H <sub>9</sub> Cl	2-Chlorobutane	53.02693	52.972	-0.00104
C <sub>4</sub> H <sub>9</sub> Cl	1-Chloro-2-methylpropane	52.99860	52.953	-0.00085
C <sub>4</sub> H <sub>9</sub> Cl	2-Chloro-2-methylpropane	53.21057	53.191	-0.00037
C <sub>5</sub> H <sub>11</sub> Cl	1-Chloropentane	65.08374	65.061	-0.00034
C <sub>5</sub> H <sub>11</sub> Cl	1-Chloro-3-methylbutane	65.15630	65.111	-0.00069
C <sub>5</sub> H <sub>11</sub> Cl	2-Chloro-2-methylbutane	65.36827	65.344	-0.00037
C <sub>5</sub> H <sub>11</sub> Cl	2-Chloro-3-methylbutane	65.16582	65.167	0.00002
C <sub>6</sub> H <sub>13</sub> Cl	2-Chlorohexane	77.34233	77.313	-0.00038
C <sub>8</sub> H <sub>17</sub> Cl	1-Chlorooctane	101.55684	101.564	0.00007
C <sub>12</sub> H <sub>25</sub> Cl	1-Chlorododecane	150.18764	150.202	0.00009
C <sub>18</sub> H <sub>37</sub> Cl	1-Chlorooctadecane	223.13384	223.175	0.00018



Table 1.7. The calculated and experimental total bond energies of alkyl bromides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CBr <sub>4</sub>	Tetrabromomethane	11.25929	11.196	-0.00566
CHBr <sub>3</sub>	Tribromomethane	12.87698	12.919	0.00323
CH <sub>3</sub> Br	Bromomethane	15.67551	15.732	0.00360
C <sub>2</sub> H <sub>5</sub> Br	Bromoethane	28.03939	27.953	-0.00308
C <sub>3</sub> H <sub>7</sub> Br	1-Bromopropane	40.19709	40.160	-0.00093
C <sub>3</sub> H <sub>7</sub> Br	2-Bromopropane	40.29798	40.288	-0.00024
C <sub>3</sub> H <sub>10</sub> Br <sub>2</sub>	2,3-Dibromo-2-methylbutane	63.48143	63.477	-0.00007
C <sub>6</sub> H <sub>13</sub> Br	1-Bromohexane	76.67019	76.634	-0.00047
C <sub>7</sub> H <sub>15</sub> Br	1-Bromoheptane	88.82789	88.783	-0.00051
C <sub>8</sub> H <sub>17</sub> Br	1-Bromooctane	100.98559	100.952	-0.00033
C <sub>12</sub> H <sub>25</sub> Br	1-Bromododecane	149.61639	149.573	-0.00029
C <sub>16</sub> H <sub>33</sub> Br	1-Bromohexadecane	198.24719	198.192	-0.00028

Table 1.8. The calculated and experimental total bond energies of alkyl iodides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CHI <sub>3</sub>	Triiodomethane	10.35888	10.405	0.00444
CH <sub>2</sub> I <sub>2</sub>	Diiodomethane	12.94614	12.921	-0.00195
CH <sub>3</sub> I	Iodomethane	15.20294	15.163	-0.00263
C <sub>2</sub> H <sub>5</sub> I	Iodoethane	27.36064	27.343	-0.00066
C <sub>3</sub> H <sub>7</sub> I	1-Iodopropane	39.51834	39.516	-0.00006
C <sub>3</sub> H <sub>7</sub> I	2-Iodopropane	39.61923	39.623	0.00009
C <sub>4</sub> H <sub>9</sub> I	2-Iodo-2-methylpropane	51.96057	51.899	-0.00119

Table 1.9. The calculated and experimental total bond energies of alkene halides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>3</sub> Cl	Chloroethene	22.46700	22.505	0.00170
C <sub>3</sub> H <sub>3</sub> Cl	2-Chloropropene	35.02984	35.05482	0.00071

Table 1.10. The calculated and experimental total bond energies of alcohols using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>4</sub> O	Methanol	21.11038	21.131	0.00097
C <sub>2</sub> H <sub>6</sub> O	Ethanol	33.40563	33.428	0.00066
C <sub>3</sub> H <sub>8</sub> O	1-Propanol	45.56333	45.584	0.00046
C <sub>3</sub> H <sub>8</sub> O	2-Propanol	45.72088	45.766	0.00098
C <sub>4</sub> H <sub>10</sub> O	1-Butanol	57.72103	57.736	0.00026
C <sub>4</sub> H <sub>10</sub> O	2-Butanol	57.87858	57.922	0.00074
C <sub>4</sub> H <sub>10</sub> O	2-Methyl-1-propananol	57.79359	57.828	0.00060
C <sub>4</sub> H <sub>10</sub> O	2-Methyl-2-propananol	58.15359	58.126	-0.00048
C <sub>5</sub> H <sub>12</sub> O	1-Pentanol	69.87873	69.887	0.00011



Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>5</sub> H <sub>12</sub> O	2-Pentanol	70.03628	70.057	0.00029
C <sub>5</sub> H <sub>12</sub> O	3-Pentanol	70.03628	70.097	0.00087
C <sub>5</sub> H <sub>12</sub> O	2-Methyl-1-butananol	69.95129	69.957	0.00008
C <sub>5</sub> H <sub>12</sub> O	3-Methyl-1-butananol	69.95129	69.950	-0.00002
C <sub>5</sub> H <sub>12</sub> O	2-Methyl-2-butananol	70.31129	70.246	-0.00092
C <sub>5</sub> H <sub>12</sub> O	3-Methyl-2-butananol	69.96081	70.083	0.00174
C <sub>6</sub> H <sub>14</sub> O	1-Hexanol	82.03643	82.054	0.00021
C <sub>6</sub> H <sub>14</sub> O	2-Hexanol	82.19398	82.236	0.00052
C <sub>7</sub> H <sub>16</sub> O	1-Heptanol	94.19413	94.214	0.00021
C <sub>8</sub> H <sub>18</sub> O	1-Octanol	106.35183	106.358	0.00006
C <sub>8</sub> H <sub>18</sub> O	2-Ethyl-1-hexanol	106.42439	106.459	0.00032
C <sub>9</sub> H <sub>20</sub> O	1-Nonanol	118.50953	118.521	0.00010
C <sub>10</sub> H <sub>22</sub> O	1-Decanol	130.66723	130.676	0.00007
C <sub>12</sub> H <sub>26</sub> O	1-Dodecanol	154.98263	154.984	0.00001
C <sub>16</sub> H <sub>34</sub> O	1-Hexadecanol	203.61343	203.603	-0.00005

Table 1.11. The calculated and experimental total bond energies of ethers using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> O	Dimethyl ether	32.84496	32.902	0.00174
C <sub>3</sub> H <sub>8</sub> O	Ethyl methyl ether	45.19710	45.183	-0.00030
C <sub>4</sub> H <sub>10</sub> O	Diethyl ether	57.54924	57.500	-0.00086
C <sub>4</sub> H <sub>10</sub> O	Methyl propyl ether	57.35480	57.355	0.00000
C <sub>4</sub> H <sub>10</sub> O	Isopropyl methyl ether	57.45569	57.499	0.00075
C <sub>6</sub> H <sub>14</sub> O	Dipropyl ether	81.86464	81.817	-0.00059
C <sub>6</sub> H <sub>14</sub> O	Disopropyl ether	82.06642	82.088	0.00026
C <sub>6</sub> H <sub>14</sub> O	t-Butyl ethyl ether	82.10276	82.033	-0.00085
C <sub>7</sub> H <sub>16</sub> O	t-Butyl isopropyl ether	94.36135	94.438	0.00081
C <sub>8</sub> H <sub>18</sub> O	Dibutyl ether	106.18004	106.122	-0.00055
C <sub>8</sub> H <sub>18</sub> O	Di-sec-butyl ether	106.38182	106.410	0.00027
C <sub>8</sub> H <sub>18</sub> O	Di-t-butyl ether	106.36022	106.425	0.00061
C <sub>8</sub> H <sub>18</sub> O	t-Butyl isobutyl ether	106.65628	106.497	-0.00218

Table 1.12. The calculated and experimental total bond energies of 1° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>5</sub> N	Methylamine	23.88297	23.857	-0.00110
C <sub>2</sub> H <sub>7</sub> N	Ethylamine	36.04067	36.062	0.00060
C <sub>3</sub> H <sub>9</sub> N	Propylamine	48.19837	48.243	0.00092
C <sub>4</sub> H <sub>11</sub> N	Butylamine	60.35607	60.415	0.00098
C <sub>4</sub> H <sub>11</sub> N	sec-Butylamine	60.45696	60.547	0.00148
C <sub>4</sub> H <sub>11</sub> N	t-Butylamine	60.78863	60.717	-0.00118
C <sub>4</sub> H <sub>11</sub> N	Isobutylamine	60.42863	60.486	0.00094



Table 1.13. The calculated and experimental total bond energies of 2° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>7</sub> N	Dimethylamine	35.76895	35.765	-0.00012
C <sub>4</sub> H <sub>11</sub> N	Diethylamine	60.22930	60.211	-0.00030
C <sub>6</sub> H <sub>15</sub> N	Dipropylamine	84.54470	84.558	0.00016
C <sub>6</sub> H <sub>15</sub> N	Diisopropylamine	84.74648	84.846	0.00117
C <sub>8</sub> H <sub>19</sub> N	Dibutylamine	108.86010	108.872	0.00011
C <sub>8</sub> H <sub>19</sub> N	Diisobutylamine	109.00522	109.106	0.00092

Table 1.14. The calculated and experimental total bond energies of 3° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>9</sub> N	Trimethylamine	47.83338	47.761	-0.00152
C <sub>6</sub> H <sub>15</sub> N	Triethylamine	84.30648	84.316	0.00012
C <sub>9</sub> H <sub>21</sub> N	Tripropylamine	120.77958	120.864	0.00070

Table 1.15. The calculated and experimental total bond energies of aldehydes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>2</sub> O	Formaldehyde	15.64628	15.655	0.00056
C <sub>2</sub> H <sub>4</sub> O	Acetaldehyde	28.18711	28.198	0.00039
C <sub>3</sub> H <sub>6</sub> O	Propanal	40.34481	40.345	0.00000
C <sub>4</sub> H <sub>8</sub> O	Butanal	52.50251	52.491	-0.00022
C <sub>4</sub> H <sub>8</sub> O	Isobutanal	52.60340	52.604	0.00001
C <sub>5</sub> H <sub>10</sub> O	Pentanal	64.66021	64.682	0.00034
C <sub>7</sub> H <sub>14</sub> O	Heptanal	88.97561	88.942	-0.00038
C <sub>8</sub> H <sub>16</sub> O	Octanal	101.13331	101.179	0.00045
C <sub>8</sub> H <sub>16</sub> O	2-Ethylhexanal	101.20587	101.259	0.00053

Table 1.16. The calculated and experimental total bond energies of ketones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>6</sub> O	Acetone	40.68472	40.672	-0.00031
C <sub>4</sub> H <sub>8</sub> O	2-Butanone	52.84242	52.84	-0.00005
C <sub>5</sub> H <sub>10</sub> O	2-Pentanone	65.00012	64.997	-0.00005
C <sub>5</sub> H <sub>10</sub> O	3-Pentanone	65.00012	64.997	-0.00005
C <sub>5</sub> H <sub>10</sub> O	3-Methyl-2-butanone	65.10101	65.036	-0.00099
C <sub>6</sub> H <sub>12</sub> O	2-Hexanone	77.15782	77.152	-0.00008
C <sub>6</sub> H <sub>12</sub> O	3-Hexanone	77.15782	77.138	-0.00025
C <sub>6</sub> H <sub>12</sub> O	2-Methyl-3-pentanone	77.25871	77.225	-0.00043
C <sub>6</sub> H <sub>12</sub> O	3,3-Dimethyl-2-butanone	77.29432	77.273	-0.00028
C <sub>7</sub> H <sub>14</sub> O	3-Heptanone	89.31552	89.287	-0.00032
C <sub>7</sub> H <sub>14</sub> O	4-Heptanone	89.31552	89.299	-0.00018
C <sub>7</sub> H <sub>14</sub> O	2,2-Dimethyl-3-pentanone	89.45202	89.458	0.00007



Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>7</sub> H <sub>14</sub> O	2,4-Dimethyl-3-pentanone	89.51730	89.434	-0.00093
C <sub>8</sub> H <sub>16</sub> O	2,2,4-Trimethyl-3-pentanone	101.71061	101.660	-0.00049
C <sub>9</sub> H <sub>18</sub> O	2-Nonanone	113.63092	113.632	0.00001
C <sub>9</sub> H <sub>18</sub> O	5-Nonanone	113.63092	113.675	0.00039
C <sub>9</sub> H <sub>18</sub> O	2,6-Dimethyl-4-heptanone	113.77604	113.807	0.00027

Table 1.17. The calculated and experimental total bond energies of carboxylic acids using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>2</sub> O <sub>2</sub>	Formic acid	21.01945	21.036	0.00079
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	33.55916	33.537	-0.00066
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Propanoic acid	45.71686	45.727	0.00022
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Butanoic acid	57.87456	57.883	0.00015
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Pentanoic acid	70.03226	69.995	-0.00053
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	3-Methylbutanoic acid	70.10482	70.183	0.00111
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	2,2-Dimethylpropanoic acid	70.31679	69.989	-0.00468
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Hexanoic acid	82.18996	82.149	-0.00050
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Heptanoic acid	94.34766	94.347	0.00000
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	Octanoic acid	106.50536	106.481	-0.00022
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	Nonanoic acid	118.66306	118.666	0.00003
C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	Decanoic acid	130.82076	130.795	-0.00020
C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	Dodecanoic acid	155.13616	155.176	0.00026
C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	Tetradecanoic acid	179.45156	179.605	0.00085
C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	Pentadecanoic acid	191.60926	191.606	-0.00002
C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	Hexadecanoic acid	203.76696	203.948	0.00089
C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	Stearic acid	228.08236	228.298	0.00094
C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	Eicosanoic acid	252.39776	252.514	0.00046

Table 1.18. The calculated and experimental total bond energies of carboxylic acid esters using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Methyl formate	32.71076	32.762	0.00156
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Methyl acetate	45.24849	45.288	0.00087
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Methyl pentanoate	81.72159	81.726	0.00005
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Methyl hexanoate	93.87929	93.891	0.00012
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	Methyl heptanoate	106.03699	106.079	0.00040
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	Methyl octanoate	118.19469	118.217	0.00018
C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	Methyl nonanoate	130.35239	130.373	0.00016
C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	Methyl decanoate	142.51009	142.523	0.00009
C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	Methyl undecanoate	154.66779	154.677	0.00006
C <sub>13</sub> H <sub>26</sub> O <sub>2</sub>	Methyl dodecanoate	166.82549	166.842	0.00010
C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	Methyl tridecanoate	178.98319	179.000	0.00009
C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	Methyl tetradecanoate	191.14089	191.170	0.00015
C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	Methyl pentadecanoate	203.29859	203.356	0.00028
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Propyl formate	57.76366	57.746	-0.00030
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Ethyl acetate	57.63888	57.548	-0.00157
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Isopropyl acetate	69.89747	69.889	-0.00013
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Ethyl propanoate	69.79658	69.700	-0.00139
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Butyl acetate	81.95428	81.873	-0.00099
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	t-Butyl acetate	82.23881	82.197	-0.00051



Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Methyl 2,2-dimethylpropanoate	82.00612	81.935	-0.00087
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Ethyl pentanoate	94.11198	94.033	-0.00084
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Ethyl 3-methylbutanoate	94.18454	94.252	0.00072
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Ethyl 2,2-dimethylpropanoate	94.39651	94.345	-0.00054
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	Isobutyl isobutanoate	106.44313	106.363	-0.00075
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	Propyl pentanoate	106.26968	106.267	-0.00003
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	Isopropyl pentanoate	106.37057	106.384	0.00013
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	Butyl pentanoate	118.42738	118.489	0.00052
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	sec-Butyl pentanoate	118.52827	118.624	0.00081
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	Isobutyl pentanoate	118.49994	118.576	0.00064

Table 1.19. The calculated and experimental total bond energies of amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> NO	Formamide	23.68712	23.697	0.00041
C <sub>2</sub> H <sub>5</sub> NO	Acetamide	36.15222	36.103	-0.00135
C <sub>3</sub> H <sub>7</sub> NO	Propanamide	48.30992	48.264	-0.00094
C <sub>4</sub> H <sub>9</sub> NO	Butanamide	60.46762	60.449	-0.00030
C <sub>4</sub> H <sub>9</sub> NO	2-Methylpropanamide	60.51509	60.455	-0.00099
C <sub>5</sub> H <sub>11</sub> NO	Pentanamide	72.62532	72.481	-0.00200
C <sub>5</sub> H <sub>11</sub> NO	2,2-Dimethylpropanamide	72.67890	72.718	0.00054
C <sub>6</sub> H <sub>13</sub> NO	Hexanamide	84.78302	84.780	-0.00004
C <sub>8</sub> H <sub>17</sub> NO	Octanamide	109.09842	109.071	-0.00025

Table 1.20. The calculated and experimental total bond energies of N-alkyl and N,N-dialkyl amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>7</sub> NO	N,N-Dimethylformamide	47.53142	47.574	0.00090
C <sub>4</sub> H <sub>9</sub> NO	N,N-Dimethylacetamide	59.91404	59.890	-0.00041
C <sub>6</sub> H <sub>13</sub> NO	N-Butylacetamide	84.63649	84.590	-0.00055

Table 1.21. The calculated and experimental total bond energies of urea using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>4</sub> N <sub>2</sub> O	Urea	31.35919	31.393	0.00108

Table 1.22. The calculated and experimental total bond energies of acid halide using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>3</sub> ClO	Acetyl chloride	28.02174	27.990	-0.00115



Table 1.23. The calculated and experimental total bond energies of acid anhydrides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	Acetic anhydride	56.94096	56.948	0.00013
C <sub>6</sub> H <sub>10</sub> O <sub>3</sub>	Propanoic anhydride	81.25636	81.401	0.00177

Table 1.24. The calculated and experimental total bond energies of nitriles using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>3</sub> N	Acetonitrile	25.72060	25.77	0.00174
C <sub>3</sub> H <sub>5</sub> N	Propanenitrile	37.87830	37.94	0.00171
C <sub>4</sub> H <sub>7</sub> N	Butanenitrile	50.03600	50.08	0.00082
C <sub>4</sub> H <sub>7</sub> N	2-Methylpropanenitrile	50.13689	50.18	0.00092
C <sub>5</sub> H <sub>9</sub> N	Pentanenitrile	62.19370	62.26	0.00111
C <sub>5</sub> H <sub>9</sub> N	2,2-Dimethylpropanenitrile	62.47823	62.40	-0.00132
C <sub>7</sub> H <sub>13</sub> N	Heptanenitrile	86.50910	86.59	0.00089
C <sub>8</sub> H <sub>15</sub> N	Octanenitrile	98.66680	98.73	0.00069
C <sub>10</sub> H <sub>19</sub> N	Decanenitrile	122.98220	123.05	0.00057
C <sub>14</sub> H <sub>27</sub> N	Tetradecanenitrile	171.61300	171.70	0.00052

Table 1.25. The calculated and experimental total bond energies of thiols using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
HS	Hydrogen Sulfide	3.77430	3.653	-0.03320
H <sub>2</sub> S	Dihydrogen Sulfide	7.56058	7.605	0.00582
CH <sub>4</sub> S	Methanethiol	19.60264	19.575	-0.00141
C <sub>2</sub> H <sub>6</sub> S	Ethanethiol	31.76034	31.762	0.00005
C <sub>3</sub> H <sub>8</sub> S	1-Propanethiol	43.91804	43.933	0.00035
C <sub>3</sub> H <sub>8</sub> S	2-Propanethiol	44.01893	44.020	0.00003
C <sub>4</sub> H <sub>10</sub> S	1-Butanethiol	56.07574	56.089	0.00024
C <sub>4</sub> H <sub>10</sub> S	2-Butanethiol	56.17663	56.181	0.00009
C <sub>4</sub> H <sub>10</sub> S	2-Methyl-1-propanethiol	56.14830	56.186	0.00066
C <sub>4</sub> H <sub>10</sub> S	2-Methyl-2-propanethiol	56.36027	56.313	-0.00084
C <sub>5</sub> H <sub>12</sub> S	2-Methyl-1-butanethiol	68.30600	68.314	0.00012
C <sub>5</sub> H <sub>12</sub> S	1-Pentanethiol	68.23344	68.264	0.00044
C <sub>5</sub> H <sub>12</sub> S	2-Methyl-2-butanethiol	68.51797	68.441	-0.00113
C <sub>5</sub> H <sub>12</sub> S	3-Methyl-2-butanethiol	68.31552	68.381	0.00095
C <sub>5</sub> H <sub>12</sub> S	2,2-Dimethyl-1-propanethiol	68.51797	68.461	-0.00084
C <sub>6</sub> H <sub>14</sub> S	1-Hexanethiol	80.39114	80.416	0.00031
C <sub>6</sub> H <sub>14</sub> S	2-Methyl-2-pentanethiol	80.67567	80.607	-0.00085
C <sub>6</sub> H <sub>14</sub> S	2,3-Dimethyl-2-butanethiol	80.71992	80.603	-0.00145
C <sub>7</sub> H <sub>16</sub> S	1-Heptanethiol	92.54884	92.570	0.00023
C <sub>10</sub> H <sub>22</sub> S	1-Decanethiol	129.02194	129.048	0.00020



Table 1.26. The calculated and experimental total bond energies of sulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> S	Dimethyl sulfide	31.65668	31.672	0.00048
C <sub>3</sub> H <sub>8</sub> S	Ethyl methyl sulfide	43.81438	43.848	0.00078
C <sub>4</sub> H <sub>10</sub> S	Diethyl sulfide	55.97208	56.043	0.00126
C <sub>4</sub> H <sub>10</sub> S	Methyl propyl sulfide	55.97208	56.029	0.00102
C <sub>4</sub> H <sub>10</sub> S	Isopropyl methyl sulfide	56.07297	56.115	0.00075
C <sub>5</sub> H <sub>12</sub> S	Butyl methyl sulfide	68.12978	68.185	0.00081
C <sub>5</sub> H <sub>12</sub> S	t-Butyl methyl sulfide	68.28245	68.381	0.00144
C <sub>5</sub> H <sub>12</sub> S	Ethyl propyl sulfide	68.12978	68.210	0.00117
C <sub>5</sub> H <sub>12</sub> S	Ethyl isopropyl sulfide	68.23067	68.350	0.00174
C <sub>6</sub> H <sub>14</sub> S	Diisopropyl sulfide	80.48926	80.542	0.00065
C <sub>6</sub> H <sub>14</sub> S	Butyl ethyl sulfide	80.28748	80.395	0.00133
C <sub>6</sub> H <sub>14</sub> S	Methyl pentyl sulfide	80.28748	80.332	0.00056
C <sub>8</sub> H <sub>18</sub> S	Dibutyl sulfide	104.60288	104.701	0.00094
C <sub>8</sub> H <sub>18</sub> S	Di-sec-butyl sulfide	104.80466	104.701	-0.00099
C <sub>8</sub> H <sub>18</sub> S	Di-t-butyl sulfide	104.90822	104.920	0.00011
C <sub>8</sub> H <sub>18</sub> S	Diisobutyl sulfide	104.74800	104.834	0.00082
C <sub>10</sub> H <sub>22</sub> S	Ethyl propyl sulfide	128.91828	128.979	0.00047
C <sub>10</sub> H <sub>22</sub> S	Diisopentyl sulfide	129.06340	129.151	0.00068

Table 1.27. The calculated and experimental total bond energies of disulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	Dimethyl disulfide	34.48127	34.413	-0.00199
C <sub>4</sub> H <sub>10</sub> S <sub>2</sub>	Diethyl disulfide	58.79667	58.873	0.00129
C <sub>6</sub> H <sub>14</sub> S <sub>2</sub>	Dipropyl disulfide	83.11207	83.169	0.00068
C <sub>8</sub> H <sub>18</sub> S <sub>2</sub>	Di-t-butyl disulfide	107.99653	107.919	-0.00072

Table 1.28. The calculated and experimental total bond energies of sulfoxides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO	Dimethyl sulfoxide	35.52450	35.435	-0.00253
C <sub>4</sub> H <sub>10</sub> SO	Diethyl sulfoxide	59.83990	59.891	0.00085
C <sub>6</sub> H <sub>14</sub> SO	Dipropyl sulfoxide	84.15530	84.294	0.00165

Table 1.29. The calculated and experimental total bond energies of sulfones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO <sub>2</sub>	Dimethyl sulfone	40.27588	40.316	0.00100



Table 1.30. The calculated and experimental total bond energies of sulfites using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO <sub>3</sub>	Dimethyl sulfite	43.95058	44.042	0.00207
C <sub>4</sub> H <sub>10</sub> SO <sub>3</sub>	Diethyl sulfite	68.54939	68.648	0.00143
C <sub>8</sub> H <sub>18</sub> SO <sub>3</sub>	Dibutyl sulfite	117.18019	117.191	0.00009

Table 1.31. The calculated and experimental total bond energies of sulfates using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO <sub>4</sub>	Dimethyl sulfate	48.70617	48.734	0.00058
C <sub>4</sub> H <sub>10</sub> SO <sub>4</sub>	Diethyl sulfate	73.30077	73.346	0.00061
C <sub>6</sub> H <sub>14</sub> SO <sub>4</sub>	Dipropyl sulfate	97.61617	97.609	-0.00008

Table 1.32. The calculated and experimental total bond energies of nitro alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> NO <sub>2</sub>	Nitromethane	25.14934	25.107	-0.00168
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	Nitroethane	37.30704	37.292	-0.00040
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	1-Nitropropane	49.46474	49.451	-0.00028
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	2-Nitropropane	49.56563	49.602	0.00074
C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	1-Nitrobutane	61.62244	61.601	-0.00036
C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	2-Nitroisobutane	61.90697	61.945	0.00061
C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>	1-Nitropentane	73.78014	73.759	-0.00028

Table 1.33. The calculated and experimental total bond energies of nitrite using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> NO <sub>2</sub>	Methyl nitrite	24.92328	24.955	0.00126

Table 1.34. The calculated and experimental total bond energies of nitrate using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> NO <sub>3</sub>	Methyl nitrate	28.18536	28.117	-0.00244
C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	Ethyl nitrate	40.34306	40.396	0.00131
C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	Propyl nitrate	52.50076	52.550	0.00093
C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	Isopropyl nitrate	52.60165	52.725	0.00233



Table 1.35. The calculated and experimental total bond energies of conjugated alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>5</sub> H <sub>8</sub>	Cyclopentene	54.83565	54.86117	0.00047
C <sub>4</sub> H <sub>6</sub>	1,3 Butadiene	42.09159	42.12705	0.00084
C <sub>5</sub> H <sub>8</sub>	1,3 Pentadiene	54.40776	54.42484	0.00031
C <sub>5</sub> H <sub>8</sub>	1,4 Pentadiene	54.03745	54.11806	0.00149
C <sub>5</sub> H <sub>6</sub>	1,3 Cyclopentadiene	49.27432	49.30294	0.00058

Table 1.36. The calculated and experimental total bond energies of aromatics and heterocyclic aromatics using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>6</sub> H <sub>6</sub>	Benzene	57.26008	57.26340	0.00006
C <sub>6</sub> H <sub>5</sub> Cl	Chlorobenzene	56.55263	56.581	0.00051
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	m-dichlorobenzene	55.84518	55.852	0.00012
C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	1,2,3-trichlorobenzene	55.13773	55.077	-0.00111
C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	1,3,5-trichlorobenzene	55.29542	55.255	-0.00073
C <sub>6</sub> Cl <sub>6</sub>	Hexachlorobenzene	52.57130	52.477	-0.00179
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	Nitrobenzene	65.18754	65.217	0.00046
C <sub>7</sub> H <sub>8</sub>	Toluene	69.48425	69.546	0.00088
C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	Benzoic acid	73.76938	73.762	-0.00009
C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>	2-chlorobenzoic acid	73.06193	73.082	0.00027
C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>	3-chlorobenzoic acid	73.26820	73.261	-0.00010
C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>	4-chlorobenzoic acid	73.26820	73.247	-0.00028
C <sub>6</sub> H <sub>7</sub> N	Aniline	64.43373	64.374	-0.00093
C <sub>7</sub> H <sub>9</sub> N	2-methylaniline	76.62345	76.643	-0.00025
C <sub>7</sub> H <sub>9</sub> N	3-methylaniline	76.62345	76.661	0.00050
C <sub>7</sub> H <sub>9</sub> N	4-methylaniline	76.62345	76.654	0.00040
C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	2-nitroaniline	72.47476	72.424	-0.00070
C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	3-nitroaniline	72.47476	72.481	-0.00009
C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	4-nitroaniline	72.47476	72.476	-0.00002
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-2-carboxylic acid	80.90857	80.941	0.00041
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-3-carboxylic acid	80.90857	80.813	-0.00118
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-4-carboxylic acid	80.90857	80.949	0.00050
C <sub>6</sub> H <sub>6</sub> O	Phenol	61.75817	61.704	-0.00087
C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>5</sub>	2,4-dinitrophenol	77.61308	77.642	0.00037
C <sub>6</sub> H <sub>8</sub> O	Anisole	73.39006	73.355	-0.00047
C <sub>10</sub> H <sub>8</sub>	Naphthalene	90.74658	90.79143	0.00049
C <sub>4</sub> H <sub>5</sub> N	Pyrrole	44.81090	44.785	-0.00057
C <sub>4</sub> H <sub>4</sub> O	Furan	41.67782	41.692	0.00033
C <sub>4</sub> H <sub>4</sub> S	Thiophene	40.42501	40.430	0.00013
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	Imidazole	39.76343	39.74106	-0.00056
C <sub>5</sub> H <sub>5</sub> N	Pyridine	51.91802	51.87927	-0.00075
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrimidine	46.57597	46.51794	-0.00125
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrazine	46.57597	46.51380	0.00095
C <sub>9</sub> H <sub>7</sub> N	Quinoline	85.40453	85.48607	0.00178
C <sub>9</sub> H <sub>7</sub> N	Isoquinoline	85.40453	85.44358	0.00046
C <sub>8</sub> H <sub>7</sub> N	Indole	78.52215	78.514	-0.00010
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	Adenine	70.83735	70.79811	-0.00055



## REFERENCES FOR SECTION IV

1. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), pp. 9-19 to 9-45.
- 5 2. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold Company, New York, New York, (1945), p. 344.
3. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), pp. 9-63; 9-64 to 9-76.
- 10 4. R. J. Fessenden, J. S. Fessenden, *Organic Chemistry*, Willard Grant Press. Boston, Massachusetts, (1979), p. 320.
5. cyclohexane at <http://webbook.nist.gov/>.
6. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold Company, New York, New York, (1945), p. 326.
- 15 7. b1 2-methyl-1-propene at <http://webbook.nist.gov/>.
8. a1 2-methyl-1-propene at <http://webbook.nist.gov/>.
9. 2-butyne at <http://webbook.nist.gov/>.
10. trifluoromethane at <http://webbook.nist.gov/>.
- 20 11. fluoroethane at <http://webbook.nist.gov/>.
12. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Krieger Publishing Company, Malabar, FL, (1991), p. 195.
13. chloromethane at <http://webbook.nist.gov/>.
14. methyl bromide at <http://webbook.nist.gov/>.
- 25 15. tetrabromomethane at <http://webbook.nist.gov/>.
16. methyl iodide at <http://webbook.nist.gov/>.
17. K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Company, New York, (1979).
18. J. Crovisier, Molecular Database—Constants for molecules of astrophysical interest in the gas phase: photodissociation, microwave and infrared spectra, Ver. 4.2, Observatoire de Paris, Section de Meudon, Meudon, France, May 2002, pp. 34–37, available at <http://www.wusr.obspm.fr/~crovisie/>.
- 30 19. methanol at <http://webbook.nist.gov/>.



20. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 46.
21. dimethyl ether at <http://webbook.nist.gov/>.
- 5 22. T. Amano, P. F. Bernath, R. W. McKellar, "Direct observation of the  $\nu_1$  and  $\nu_3$  fundamental bands of  $NH_2$  by difference frequency laser spectroscopy", *J. Mol. Spectrosc.*, Vol. 94, (1982), pp. 100-113.
23. methylamine at <http://webbook.nist.gov/>.
24. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 79th Edition, CRC Press, Boca  
10 Raton, Florida, (1998-9), pp. 9-80 to 9-85.
25. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 482.
26. acetaldehyde at <http://webbook.nist.gov/>.
- 15 27. acetone at <http://webbook.nist.gov/>.
28. 2-butanone at <http://webbook.nist.gov/>.
29. acetic acid at <http://webbook.nist.gov/>.
30. formic acid at <http://webbook.nist.gov/>.
31. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and  
20 Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 138.
32. methyl formate at <http://webbook.nist.gov/>.
33. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and  
25 Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 144.
34. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 147.
35. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and  
30 Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 143.



36. H. J. Vledder, F. C. Mijlhoff, J. C. Leyte, C. Romers, "An electron diffraction investigation of the molecular structure of gaseous acetic anhydride", *Journal of Molecular Structure*, Vol. 7, Issues 3-4, (1971), pp. 421-429.
37. acetonitrile at <http://webbook.nist.gov/>.
- 5 38. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), pp. 10-202 to 10-204.
39. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), p. 9-79.
40. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Taylor & Francis, Boca Raton, (2005-6), pp. 9-82 to 9-86.
- 10 41. thiirane at <http://webbook.nist.gov/>.
42. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 242.
- 15 43. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 241.
44. R. M. Ibberson, M. T. F. Telling, S. Parsons, "Structural determination and phase transition behavior of dimethyl sulfate", *Acta. Cryst.*, Vol. B62, (2006), pp. 280-286.
- 20 45. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 181.
46. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 480.
- 25 47. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 187.
48. 1,3-butadiene at <http://webbook.nist.gov/>.
- 30 49. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold Company, New York, New York, (1945), pp. 362-369.



50. W. I. F. David, R. M. Ibberson, G. A. Jeffrey, J. R. Ruble, "The structure analysis of deuterated benzene and deuterated nitromethane by pulsed-neutron powder diffraction: a comparison with single crystal neutron analysis", *Physica B* (1992), 180 & 181, pp. 597-600..
- 5 51. G. A. Jeffrey, J. R. Ruble, R. K. McMullan, J. A. Pople, "The crystal structure of deuterated benzene," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Vol. 414, No. 1846, (Nov. 9, 1987), pp. 47-57.
52. H. B. Burgi, S. C. Capelli, "Getting more out of crystal-structure analyses," *Helvetica Chimica Acta*, Vol. 86, (2003), pp. 1625-1640.
- 10 53. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 481.
54. R. Boese, D. Blaser, M. Nussbaumer, T. M. Krygowski, "Low temperature crystal and molecular structure of nitrobenzene", *Structural Chemistry*, Vol. 3, No. 5, (1992), pp. 363-368.
- 15 55. G. A. Sim, J. M. Robertson, T. H. Goodwin, "The crystal and molecular structure of benzoic acid", *Acta Cryst.*, Vol. 8, (1955), pp.157-164
56. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 301.
- 20 57. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 303.
58. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 207.
- 25 59. S. Martinez-Carrera, "The crystal structure of Imidazole at -150°C", *Acta. Cryst.*, Vol. 20, (1966), pp. 783-789.
60. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, *The Handbook of Infrared and Raman Frequencies of Organic Molecules*, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), pp. 296-297.
- 30



61. H. Sternglanz, C. E. Bugg, "Conformations of N<sup>6</sup>-monosubstituted adenine derivatives  
crystal structure of N<sup>6</sup>-methyladenine", *Biochimica et Biophysica Acta*, Vol. 308, (1973),  
pp. 1-8.



## Section V1

## Software Program

The present invention relates to a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising: processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

In one embodiment, for example, the system comprises five components: (1) the graphical user interface (GUI); (2) the routine for parsing between an input chemical structure or name and taking the input and activating a routine to call up the parts of the molecule (functional groups), which are used for determining the energies and structure to be rendered; (3) the functional-group data base that has an organization of the theoretical solutions; (4) the rendering engine, which calculates and enables manipulations of the image, such as a three-dimensional model in response to commands, as well as responds to commands for data parameters corresponding to the image such as bond energies and charge distribution and geometrical parameters; and (5) data transfer system for inputting numerical data into or out of the computational components and storage components of the main system. The system further comprises spreadsheets with solutions of the bond parameters with output in any standard spreadsheet format. The system also comprises a data-handling program to transfer data from the spreadsheets into the main program.

The output may be, for example, at least one of graphical, simulation, text, and numerical data. The output may be the calculation of at least one of: (1) a bond distance between two atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.



In other embodiments, the charge, current, energy, and geometrical parameters are output to be inputs to other programs that may be used in further applications. For example, the data of heats of formation may be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways. That is, a novel composition of matter may be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The charge and current density functions may be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species. These fields and the predictions of field interactions may be computed using Maxwell's equations. In one embodiment, finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index. Furthermore, the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization. Furthermore, the data can be input into other programs of the system, which calculate thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

The output data may be used to predict a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The novel property, for example, may be a new pharmaceutical use, or stability at room temperature of a novel arrangement of atoms or ions.

In one embodiment, the output device of the system is a display that displays at least one of visual or graphical media. The display may be at least one of static or dynamic. At least one of vibration, rotation, and translation may be displayed. The displayed information



may be used for at least one of modeling reactivity, predicting physical properties, and aiding in drug and material design. The output device may be a monitor, video projector, printer, or one-, two- or three-dimensional rendering device. The displayed information may be used to model other molecules and provides utility to anticipate their reactivity and physical properties.

5 Additionally, data may be output and used in the same and additional applications as the rendered models and representations of the calculated physical solutions. The processing means of the system may be a general-purpose computer. The general-purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input  
10 means. The input means may comprise a serial port, USB port, microphone input, camera input, keyboard or mouse. The processing means comprises a special purpose computer or other hardware system. The system may comprise computer program products such as computer readable medium having embodied therein program code means. The computer readable media may be any available media which can be accessed by a general purpose or  
15 special purpose computer. The computer readable media may comprise, for example, at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium that can embody the desired program code means and which can be accessed by a general purpose or special purpose computer. The program code means may comprise executable instructions and data, which  
20 cause a general purpose computer or special purpose computer to perform a certain function of a group of functions. Commercial examples of suitable program language includes, for example, C++, C, JAVA, FORTRAN, Python and Assembly Languages, programmed with an algorithm based on the physical solutions, and the computer may be a PC, mainframe, supercomputer, or cluster of computers. Commercial examples of suitable programs include,  
25 for example, APIs like OpenGL, DirectX, FOX GUI toolkit, and Qt. This program may be developed to run on at least one of operating systems like Windows XP, Windows 2000, Windows Vista, MAC OS, MAC OS X, Linux, Unix, Irix and other Unix-type operating systems.

Millsian software is designed to render 3-D models of molecules, molecular ions,  
30 molecular radicals, functional groups thereof, and related structure and property information and produce useful data output and application of the parameters of these species, wherein the nature of their bound electrons and chemical bonds are solved using Dr. Randell L. Mills' Classical Quantum Mechanics theory described in the reference: R. L. Mills, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional



Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at

<http://www.blacklightpower.com/bookdownload.shtml>, which is incorporated by this reference in its entirety. Figure 76 provides a flow chart diagram, which is an example of a software

5 system that can be utilized for this purpose, which example is not intended to limit the scope of the disclosed inventions. The main parts of this exemplary software system illustrated in Figure 76 will now be further explained:

Start: A user can start the program by running an executable program file. That might  
10 be done, for example, by double clicking the program icon on a Windows-based operating system, or typing the name of the executable file on the command line and pressing the 'Enter' key on a Linux or Unix operating system. The program initially starts by reading data files located in specific directories. The names of those directories and locations are fixed according to the type and format of the data files.

15 Data files: There are two types of data files used in the software system: functional group data files and molecule data files. Functional group data files contain information about various functional groups. Functional groups are the basic bonding elements or units that each typically comprise an atom, or at least two atoms bound together as found within a molecule (e.g. -Cl, C=C, C=O, CH<sub>3</sub>). Functional groups typically dictate or define properties and  
20 structure of the molecule. Similar functional groups in different molecules typically react in similar ways when subjected to a particular set of reaction conditions. Molecule data files contain information about molecules, molecular ions, and molecular radicals. These data files are processed according to their file formats.

File formats: Millsian software employs two kinds of file formats for storing  
25 information about the structure, energies and names of molecules and functional groups: raw-data format and hierarchical format. In a raw-data file, all information is stored as is, below the header describing the type of information. As shown in the Table below, for example, the names of the molecule or functional group are listed below the #NAMES header. The names and positions of the atoms are listed below the #ATOMS header, and so on.



```

#NAMES
CH3
Alkane CH3

#SMILES
C-

#ATOMS
1      C      0      0      0
2      H      1.9775 -0.698 0
3      H      -0.9888      -0.698 1.712
4      H      -0.9888      -0.698 -1.712

#AO
1      1 1s    0.171 2
2      1 2sp3  0.864 -1

#BONDS
1      1 2      1      1.649
2      1 3      1      1.649
3      1 4      1      1.649

#BONDAXES
1      1      1      90      0      0

#DATA
RCH bond angle: 109.44°
CH bond length: 2.097 a
HFORM: 12.492

```

Most of the functional groups files and some simple molecule files are stored in raw data format. The other file format used with the Millsian software system, the hierarchical file format, represents the information in a graph style, in which nodes are connected to other nodes through links. This format is designed to construct molecules by attaching different functional groups in a desired manner. Using this file format, the user can construct complex molecules built from solved functional groups.

For example, as shown in the Table below, the pentane data file includes a #GROUPS header below which is list all of the functional groups that form a part of the pentane molecule. Under the #GROUP\_LINKS header is information about how these functional groups are connected to each other to construct pentane.



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```
#NAMES
Pentane

#SMILES
CCCCC

#GROUPS
1      C-
2      -C-
3      -C-
4      -C-
5      C-

#GROUP_LINKS
1      1 1      2 1      180
2      2 2      3 1      180
3      3 2      4 1      180
4      4 2      5 1      180
```

- 15 Processing data files: As further shown in the flow diagram of Figure 76 for the exemplary Millsian software system, the program first processes the functional group data file and constructs the functional-group objects, which are complete 3-D representations of the functional groups and their related information supplied in the corresponding file. These objects are then ready to be visually displayed through use of a molecule viewer. Next, the
- 20 program processes the molecule data file. If the molecule data file is in raw-data format, then the program makes a molecule object directly from it. If the file is in hierarchical format, then the program calculates geometric parameters from listed functional groups. The program stores all functional-group objects and molecule objects using internal data structures.
- 25 Visualization/ User Interactions: As shown in Figures 77 and 78, the molecule viewer displays the functional-group objects and molecule objects and provides basic interaction capabilities with the displayed objects, such as rotating, scaling, and moving the objects. The molecule viewer also provides other visualization options, such as viewing molecules in wire frame mode, viewing coordinate axes, and changing of the transparency and lighting. The
- 30 user, for example, can also select parts of a molecule for visualization, like a nucleus, atomic orbital, molecular orbital, or bond axis. The viewer also includes a drop down information window, which provides, for example, related information about molecules, such as bond angles, component functional groups, and total heat of formation. In one embodiment, a user can create new molecules by joining functional groups. For this purpose, the user can select a



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first functional group. Next, the user can select an open bond from the functional group where the user desires to attach another group. Next, the user can select another or the same functional group, followed by selecting an open bond from the other group. The user can join the two selected functional groups at the selected open bonds by clicking on 'Join Groups'.

- 5 This method of joining functional groups at open bonds can be repeated to form the desired molecule.

SMILES input: The Simplified Molecular Input Line Entry Specification or SMILES is a specification for unambiguously describing the structure of chemical molecules using short ASCII strings. Through the user interface, a user can enter SMILES to construct molecules,

- 10 provided the new molecule comprises functional groups that are in the database. Once a SMILES is entered, a parser reads in and breaks it down into component functional groups. The software system then attaches the component functional groups to create the new molecule object, which can then be viewed using the molecule viewer.

- While the claimed invention has been described in detail and with reference to specific  
15 embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.



CONTINUOUS-CHAIN ALKANES ( $C_nH_{2n+2}$ ,  $n = 3, 4, 5 \dots \infty$ )

The continuous-chain alkanes,  $C_nH_{2n+2}$ , are the homologous series comprising terminal methyl groups at each end of the chain with  $n - 2$  methylene ( $CH_2$ ) groups in between:



5  $C_nH_{2n+2}$  can be solved using the same principles as those used to solve ethane and ethylene wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three  $H$  AOs combine with three carbon  $2sp^3$  HOs and two  $H$  AOs combine with  
 10 two carbon  $2sp^3$  HOs to form each methyl and methylene group, respectively, where each bond comprises a  $H_2$ -type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The  $CH_3$  and  $CH_2$  groups bond by forming  $H_2$ -type MOs between the remaining  $C2sp^3$  HOs on the carbons such that each carbon forms four bonds involving its four  $C2sp^3$  HOs. For the alkyl  $C-C$  group,  $E_T(atom - atom, msp^3.AO)$  is  
 15  $-1.85836 \text{ eV}$  where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the chain comprising methylene groups and terminal methyl groups.

The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of straight-chain alkanes are given in Tables 15.4,  
 20 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.8. In this angle table and those given in subsequent sections when  $c'_2$  is given as the ratio of two values of  
 25  $c_2$  designated to Atom 1 and Atom 2 and corresponding to  $E_{Coulombic}$  of Atom 1 and Atom 2,

$$\text{respectively, then } c'_2 = \frac{c_2(Atom\ 2)}{c_2(Atom\ 1)}.$$



Table 15.4. The geometrical bond parameters of straight-chain alkanes and experimental values [1].

Parameter	C'-C' Group	C'-H (CH <sub>3</sub> ) Group	C'-H (CH <sub>2</sub> ) Group
$a$ (a <sub>0</sub> )	2.12499	1.64920	1.67122
$c'$ (a <sub>0</sub> )	1.45744	1.04856	1.05553
Bond Length 2c' (Å)	1.54280	1.10974	1.11713
Exp. Bond Length (Å)	1.532 (propane) 1.531 (butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)
$h, c$ (a <sub>0</sub> )	1.54616	1.27295	1.29569
$\sigma$	0.68600	0.63580	0.63159

Table 15.5. The MO to HO intercept geometrical bond parameters of straight-chain alkanes.  $E_r$  is  $E_r(atom - atom, nsp^3, AC)$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy C2sp <sup>3</sup> (eV)	$r_{final}$ (a <sub>0</sub> )	$r_{bond}$ (a <sub>0</sub> )	$E_{r_{intercept}}$ (eV) Final	$E$ (C2sp <sup>3</sup> ) (eV) Final	$\theta'$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
C-H (CH <sub>3</sub> )	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18703
C-H (CH <sub>2</sub> )	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
H <sub>3</sub> C-C <sub>2</sub> H <sub>4</sub> CH <sub>2</sub>	C <sub>2</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
H <sub>3</sub> C-C <sub>2</sub> H <sub>4</sub> CH <sub>2</sub>	C <sub>3</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117



Table 15.6. The energy parameters (eV) of functional groups of straight-chain alkanes.

Parameters	C – C Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group
$n_1$	1	3	2
$n_2$	0	2	1
$n_3$	0	0	0
$C_1$	0.5	0.75	0.75
$C_2$	1	1	1
$c_1$	1	1	1
$c_2$	0.91771	0.91771	0.91771
$c_3$	0	0	1
$c_4$	2	1	1
$c_5$	0	3	2
$C_{1o}$	0.5	0.75	0.75
$C_{2o}$	1	1	1
$V_e$ (eV)	-28.79214	-107.32728	-70.41425
$V_p$ (eV)	9.33352	38.92728	25.78002
$T$ (eV)	6.77464	32.53914	21.06675
$V_m$ (eV)	-3.38732	-16.26957	-10.53337
$E_{(AO/HO)}$ (eV)	-15.56407	-15.56407	-15.56407
$\Delta E_{H_2MO(AO/HO)}$ (eV)	0	0	0
$E_T(AO/HO)$ (eV)	-15.56407	-15.56407	-15.56407
$E_T(H_2MO)$ (eV)	-31.63537	-67.69451	-49.66493
$E_T(atom - atom, msp^3.AO)$ (eV)	-1.85836	0	0
$E_T(MO)$ (eV)	-33.49373	-67.69450	-49.66493
$\omega$ ( $10^{15}$ rad / s)	9.43699	24.9286	24.2751
$E_K$ (eV)	6.21159	16.40846	15.97831
$\bar{E}_D$ (eV)	-0.16515	-0.25352	-0.25017
$\bar{E}_{Kvib}$ (eV)	0.12312 [2]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))
$\bar{E}_{osc}$ (eV)	-0.10359	-0.22757	-0.14502
$E_{mag}$ (eV)	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-33.59732	-67.92207	-49.80996
$E_{initial}(c_1 AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5 AO/HO)$ (eV)	0	-13.59844	-13.59844
$E_D(Group)$ (eV)	4.32754	12.49186	7.83016



Table 15.7 The total bond energies of n-alkanes calculated using the functional group composition and the energies of Table 15.6 compared to the experimental values [3].

Formula	Name	C-C	CH <sub>3</sub>	CH <sub>2</sub>	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>8</sub>	Propane	2	2	1	41.4896	41.434	-0.00085
C <sub>4</sub> H <sub>10</sub>	Butane	3	2	2	53.62666	53.61	-0.00036
C <sub>5</sub> H <sub>12</sub>	Pentane	4	2	3	65.78436	65.77	-0.00017
C <sub>6</sub> H <sub>14</sub>	Hexane	5	2	4	77.94206	77.93	-0.00019
C <sub>7</sub> H <sub>16</sub>	Heptane	6	2	5	90.09976	90.09	-0.00013
C <sub>8</sub> H <sub>18</sub>	Octane	7	2	6	102.25746	102.25	-0.00006
C <sub>9</sub> H <sub>20</sub>	Nonane	8	2	7	114.41516	114.40	-0.00012
C <sub>10</sub> H <sub>22</sub>	Decane	9	2	8	126.57286	126.57	-0.00003
C <sub>11</sub> H <sub>24</sub>	Undecane	10	2	9	138.73056	138.736	0.00004
C <sub>12</sub> H <sub>26</sub>	Dodecane	11	2	10	150.88826	150.88	-0.00008
C <sub>18</sub> H <sub>38</sub>	Octadecane	18	2	16	223.83446	223.85	0.00008

Table 15.8. The bond angle parameters of straight-chain alkanes and experimental values [1]. In the calculation of  $\theta_v$ , the parameters from the preceding angle were used.  $E_\tau$  is  $E_\tau(\text{atom} - \text{atom}, \text{msp}^3.AO)$ .

[illegible]



BRANCHED ALKANES ( $C_nH_{2n+2}$ ,  $n = 3, 4, 5 \dots \infty$ )

The branched-chain alkanes,  $C_nH_{2n+2}$ , comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those used to solve the methyl and methylene functional groups wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom, msp^3.AO)$  of each  $C-C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is  $-1.85836 eV$  or  $-1.44915 eV$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 eV$  (Eq. (14.513), or methyl,  $-0.72457 eV$  (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each  $E_D(group)$  of Table 15.12 corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.14.



Table 15.9. The symbols of functional groups of branched alkanes.

Functional Group	Group Symbol
CH <sub>3</sub> group	$C - H (CH_3)$
CH <sub>2</sub> group	$C - H (CH_2)$
CH	$C - H$
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 15.10. The geometrical bond parameters of branched alkanes and experimental values [1].

Parameter	C—H ( $\text{C}^1\text{H}_3$ ) Group	C—H ( $\text{C}^2\text{H}_2$ ) Group	C—C (a) Group	C—C (b) Group	C—C (c) Group	C—C (d) Group	C—C (e) Group	C—C (f) Group
$a$ ( $a_0$ )	1.64920	1.67122	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ ( $a_0$ )	1.04856	1.05553	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ( $\text{\AA}$ )	1.0974	1.11713	1.54280	1.54280	1.55635	1.54280	1.53635	1.53635
Exp. Bond Length ( $\text{\AA}$ )	1.107 (C—H propane) 1.117 (isobutane) 1.107 (C—H butane)	1.107 (C—H propane) 1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c$ ( $a_0$ )	1.27295	1.29569	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$a$	0.63380	0.63159	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.11. The MO to HO intercent geometrical bond parameters of branched-chain alkanes.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, A^\circ)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy ( $C_{2vp}$ ) (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{atom}}$ ( $a_0$ )	$E_{\text{intercept}}(C_{2vp})$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H(CH_3)$	C	-0.92018	0	0	0	-152.54487	0.91771	0.86359	-15.75493	77.49	102.51	41.48	1.23564	0.18708
$C-H(CH_2)$	C	-0.92018	-0.92018	0	0	-153.47406	0.91771	0.81549	-16.68412	68.47	111.53	35.84	1.35486	0.29933
$C-H(CH)$	C	-0.92018	-0.92018	-0.92018	0	-154.40324	0.91771	0.77247	-17.61330	61.10	118.90	31.37	1.42988	0.37326
$H_2C-C(H_2)CH_2$	C <sub>u</sub>	-0.92018	0	0	0	-152.54487	0.91771	0.86359	-15.75493	63.82	116.18	30.08	1.83879	0.38106
$H_2C-C(H_2)CH_2$ (C-C (a))	C <sub>b</sub>	-0.92018	-0.92018	0	0	-153.47406	0.91771	0.81549	-16.68412	56.41	122.59	26.06	1.90890	0.51517
$R-H_2C-C(H_2)(H_2C-R')HCH_2$ (C-C (a))	C <sub>b</sub>	-0.92018	-0.92018	-0.92018	0	-154.40324	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C-C(R''-H_2C)C(R''-H_2C)CH_2$ (C-C (b))	C <sub>b</sub>	-0.92018	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	48.21	131.79	21.74	1.95734	0.50570
$isoC_4H_9(H_2C-R')HCH_2$ (C-C (c))	C <sub>b</sub>	-0.92018	-0.92018	-0.92018	0	-154.40324	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$isoC_4H_9(R''-H_2C)C(R''-H_2C)CH_2$ (C-C (d))	C <sub>b</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	50.04	129.96	22.66	1.94462	0.49298
$isoC_4H_9(H_2C-R')HCH_2$ (C-C (e))	C <sub>b</sub>	-0.72457	-0.92018	-0.92018	0	-154.19863	0.91771	0.78155	-17.40869	52.78	127.22	24.04	1.92443	0.47279
$isoC_4H_9(R''-H_2C)C(R''-H_2C)CH_2$ (C-C (f))	C <sub>b</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	50.04	129.96	22.66	1.94462	0.49298



Table 15.12. The energy parameters (eV) of functional groups of branched-chain alkanes.

Parameters	$CH_3$ Group	$CH_2$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$\eta_1$	3	2	1	1	1	1	1	1	1
$\eta_2$	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0
$C_1$	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1
$c_1$	1	1	1	1	1	1	1	1	1
$c_2$	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$c_3$	0	1	1	0	0	0	1	1	0
$c_4$	1	1	1	2	2	2	2	2	2
$c_5$	3	2	1	0	0	0	0	0	0
$C_{10}$	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{30}$	1	1	1	1	1	1	1	1	1
$V_r$ (eV)	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p$ (eV)	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T$ (eV)	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_a$ (eV)	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E'_{\text{atom}}$ (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_{1,2,3}}(atom)$ (eV)	0	0	0	0	0	0	0	0	0
$E_T(1,atom)$ (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(1,2,atom)$ (eV)	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(1,atom, msp, AO)$ (eV)	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(1,2,atom)$ (eV)	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^{15}$ rad/s)	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_k$ (eV)	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_n$ (eV)	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{\text{rot}}$ (eV)	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{\text{osc}}$ (eV)	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{\text{mag}}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(1,2,atom)$ (eV)	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{\text{rot}}$ ( $\omega, atom$ ) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{rot}}$ ( $\omega, atom$ ) (eV)	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(1,2,atom)$ (eV)	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734



Table 15.13. The total bond energies of branched alkanes calculated using the functional group composition and the energies of Table 15.12 compared to the experimental values [3].

Formula	Name	CH <sub>3</sub>	CH <sub>2</sub>	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>4</sub> H <sub>10</sub>	Isobutane	3	0	1	0	3	0	0	0	0	53.69922	53.695	-0.00007
C <sub>5</sub> H <sub>12</sub>	Isopentane	3	1	1	1	3	0	0	0	0	65.85692	65.843	-0.00021
C <sub>5</sub> H <sub>12</sub>	Neopentane	4	0	0	0	0	4	0	0	0	65.86336	65.992	0.00195
C <sub>6</sub> H <sub>14</sub>	2-Methylpentane	3	2	1	2	3	0	0	0	0	78.01462	78.007	-0.00010
C <sub>6</sub> H <sub>14</sub>	3-Methylpentane	3	2	1	2	3	0	0	0	0	78.01462	77.979	-0.00046
C <sub>6</sub> H <sub>14</sub>	2,2-Dimethylbutane	4	1	0	1	0	4	0	0	0	78.02106	78.124	0.00132
C <sub>6</sub> H <sub>14</sub>	2,3-Dimethylbutane	4	1	0	0	0	4	1	0	0	77.99581	78.043	0.00061
C <sub>6</sub> H <sub>16</sub>	2-Methylhexane	3	3	1	3	3	0	0	0	0	90.17232	90.160	-0.00014
C <sub>6</sub> H <sub>16</sub>	3-Methylhexane	3	3	1	3	3	0	0	0	0	90.17232	90.127	-0.00051
C <sub>6</sub> H <sub>16</sub>	3-Ethylpentane	3	3	1	3	3	0	0	0	0	90.17232	90.108	-0.00072
C <sub>6</sub> H <sub>16</sub>	2,2-Dimethylpentane	4	2	0	2	0	4	0	0	0	90.17876	90.276	0.00107
C <sub>6</sub> H <sub>16</sub>	2,3-Dimethylpentane	4	2	0	2	0	3	0	0	1	90.22301	90.262	0.00044
C <sub>6</sub> H <sub>16</sub>	2,4-Dimethylpentane	4	1	2	0	0	0	0	0	0	90.24488	90.233	-0.00013
C <sub>6</sub> H <sub>16</sub>	3,3-Dimethylpentane	4	2	0	2	0	4	0	0	0	90.17876	90.227	0.00054
C <sub>6</sub> H <sub>18</sub>	2-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.322	-0.00008
C <sub>6</sub> H <sub>18</sub>	3-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.293	-0.00036
C <sub>6</sub> H <sub>18</sub>	4-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.286	-0.00043
C <sub>6</sub> H <sub>18</sub>	2,2-Dimethylhexane	4	3	0	3	0	4	0	0	0	102.30169	102.274	-0.00027
C <sub>6</sub> H <sub>18</sub>	2,3-Dimethylhexane	4	2	2	2	4	0	0	0	0	102.33646	102.417	0.00079
C <sub>6</sub> H <sub>18</sub>	2,4-Dimethylhexane	4	2	2	1	6	0	0	0	0	102.31121	102.306	-0.00005
C <sub>6</sub> H <sub>18</sub>	2,5-Dimethylhexane	4	2	2	1	6	0	0	0	0	102.40258	102.362	-0.00040
C <sub>6</sub> H <sub>18</sub>	3,3-Dimethylhexane	4	3	0	3	0	4	0	0	0	102.40258	102.396	-0.00006
C <sub>6</sub> H <sub>18</sub>	3,4-Dimethylhexane	4	2	2	2	4	0	0	0	0	102.33646	102.369	0.00032
C <sub>6</sub> H <sub>18</sub>	3-Ethyl-2-methylpentane	4	2	2	2	4	0	0	0	0	102.31121	102.296	-0.00015
C <sub>6</sub> H <sub>18</sub>	3-Ethyl-3-methylpentane	4	3	0	3	0	1	0	0	0	102.31121	102.277	-0.00033
C <sub>6</sub> H <sub>18</sub>	2,2,3-Trimethylpentane	5	1	1	1	2	3	0	0	1	102.33646	102.317	-0.00019
C <sub>6</sub> H <sub>18</sub>	2,2,4-Trimethylpentane	5	1	1	1	2	3	0	0	0	102.38071	102.370	-0.00010
C <sub>6</sub> H <sub>18</sub>	2,3,3-Trimethylpentane	5	0	0	0	3	0	0	0	0	102.40902	102.412	0.00003
C <sub>6</sub> H <sub>18</sub>	2,3,4-Trimethylpentane	5	0	0	0	5	0	0	0	0	102.38071	102.332	-0.00048
C <sub>6</sub> H <sub>18</sub>	2,2,3,3-Tetramethylbutane	6	0	0	0	0	6	0	0	0	102.29240	102.342	0.00049
C <sub>6</sub> H <sub>20</sub>	2,3,5-Trimethylhexane	5	1	3	0	7	0	1	0	0	102.41632	102.433	0.00016
C <sub>6</sub> H <sub>20</sub>	3,3-Diethylpentane	4	4	0	4	0	0	0	0	0	114.54147	114.551	0.00008
C <sub>6</sub> H <sub>20</sub>	2,2,3,3-Tetramethylpentane	6	1	0	0	0	4	0	0	0	114.49416	114.455	-0.00034
C <sub>6</sub> H <sub>20</sub>	2,2,3,4-Tetramethylpentane	6	0	0	0	3	3	0	1	0	114.57402	114.494	-0.00070
C <sub>6</sub> H <sub>20</sub>	2,2,4,4-Tetramethylpentane	6	1	0	0	0	8	0	0	1	114.51960	114.492	-0.00024
C <sub>6</sub> H <sub>20</sub>	2,3,3,4-Tetramethylpentane	6	0	0	0	0	2	0	0	2	114.57316	114.541	-0.00028
C <sub>6</sub> H <sub>22</sub>	2-Methylheptane	3	6	1	6	3	0	0	0	0	114.58266	114.484	-0.00086
C <sub>6</sub> H <sub>22</sub>	5-Methylheptane	3	6	1	6	3	0	0	0	0	126.64542	126.680	0.00027
C <sub>10</sub> H <sub>22</sub>		3				3				0	126.64542	126.663	0.00014



Table 15.14. The bond angle parameters of branched-chain alkanes and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

Atoms of Angle	$2c'_1$ Bond 1 ( $a_1$ )	$2c'_2$ Bond 2 ( $a_2$ )	$2c'_3$ Terminal Atoms ( $a_3$ )	$E_{terminal}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c'_2$	$E_T$ (eV)	$\theta_i$ ( $^\circ$ )	$\theta_j$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
Methylane $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	0.86359	1	1	0.75	1.15796	0			108.44	107 (propane)
$\angle C_aC_bC_c$													69.51		110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$													69.51		110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	0.86359	1	1	0.75	1.15796	0			109.50	
$\angle C_aC_bC_c$													70.56		109.44	
$\angle C_aC_bH$													70.56		109.44	
$\angle C_aC_bC_c$ iso $C_a$	2.91547	2.91547	4.7958	-16.68412 $C_b$	25		0.81549	1	1	1	0.81549	-1.85836			110.67	110.8 (isobutane)
$\angle C_aC_bH$ iso $C_a$	2.91547	2.11323	4.1633	-15.55033 $C_n$	5		0.87495	0.91771	1	0.75	1.04887	0			110.76	
$\angle C_aC_bH$ iso $C_a$	2.91547	2.09711	4.1633	-15.55033 $C_b$	5		0.87495	0.91771	1	0.75	1.04887	0			111.27	111.4 (isobutane)
$\angle C_aC_bC_c$ tert $C_a$	2.90327	2.90327	4.7958	-15.55033 $C_h$	5		0.87495	0.91771	1	0.75	1.04887	-1.85836			111.27	111.4 (isobutane)
$\angle C_aC_bC_d$													72.50		107.50	



# ALKENES ( $C_nH_{2n}$ , $n = 3, 4, 5 \dots \infty$ )

The straight and branched-chain alkenes,  $C_nH_{2n}$ , comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified:  $C$  vinyl single bond to  $-C(C)=C$ ,  $C$  vinyl single bond to  $-C(H)=C$ , and  $C$  vinyl single bond to  $-C(C)=CH_2$ . In addition,  $CH_2$  of the  $-C=CH_2$  moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom,msp^3.AO)$  of the  $C=C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is equivalent to that of ethylene,  $-2.26759 eV$ , given by Eq. (14.247).  $E_r(atom-atom,msp^3.AO)$  of each  $C-C$ -bond MO in Eq. (15.52) is  $-1.85836 eV$  or  $-1.44915 eV$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 eV$  (Eq. (14.513), or methyl,  $-0.72457 eV$  (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.71-15.78)), and energy (Eqs.



(15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage 5, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $eV$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of alkenes determined using Eqs. (15.79-15.108) are given in Table 15.20.







Table 15.17. The MO to HO intercept geometrical bond parameters of alkenes.  $R_1$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $C2sp^2$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{C2sp}^2}$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C_1(H)C_2 = C_3(H)C_4$	$C_2$	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	127.61	52.39	58.24	0.77492	0.49168
$C_2(H)C_3 = C_4(H)C_5$	$C_3$	-1.13380	0	0	0	-152.70949	0.91771	-15.95955	120.84	50.16	60.70	0.72040	0.54620
$C_3(C_4)C_2 = C_4(H)C_5$	$C_4$	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	-17.08869	126.39	53.61	56.95	0.80289	0.46371
$R_1C_1(H)C_2 = C_3(C)C_4$	$C_3$	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	-17.08869	60.88	119.12	27.79	1.81127	0.38039
$R_1C_1(H)C_2 = C_3(C)C_4$	$C_4$	-0.72457	-0.92918	0	0	-153.26945	0.91771	-16.47951	67.40	112.60	31.36	1.74821	0.31734
$R_1C_1(H)C_2 = C_3(C)C_4$	$C_2$	-1.13380	-0.92918	0	0	-153.67866	0.91771	-16.88873	64.57	115.43	29.79	1.77684	0.34596
$R_1C_1(H)C_2 = C_3(H)C_4$	$C_3$	-0.92918	-0.92918	0	0	-153.47405	0.91771	-16.68411	65.99	114.01	30.58	1.76270	0.33183
$C - H(C_2)(C_1)$	$C$	-1.13380	0	0	0	-152.74949	0.91771	-15.95955	77.15	102.85	41.13	1.23531	0.18965
$C - H(C_2)(C_1)$	$C$	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	77.49	102.51	41.48	1.23564	0.18708
$C - H(C_2)(C_1)$	$C$	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	68.47	111.53	35.84	1.35486	0.29933
$H_1C_1C_2H_1C_2 -$ $(C - C)(e)$	$C_1$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	61.10	118.90	31.37	1.42988	0.37326
$H_1C_1C_2H_1C_2 -$ $(C - C)(e)$	$C_2$	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	63.82	116.18	30.08	1.83879	0.38106
$R - H_2C_1C_2(H_2C_2 - R)HC(H_2 -$ $(C - C)(e))$	$C_1$	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	56.41	123.59	26.06	1.98890	0.45117
$R - H_2C_1C_2(H_2C_2 - R)HC(H_2 -$ $(C - C)(e))$	$C_2$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_1C_2(H_2C_2 - R)HC(H_2 -$ $(C - C)(e))$	$C_3$	-0.92918	-0.72457	-0.72457	-0.72457	-154.17860	0.91771	-17.92866	48.21	131.79	21.74	1.95734	0.50570
$R - H_2C_1C_2(H_2C_2 - R)HC(H_2 -$ $(C - C)(e))$	$C_4$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_1C_2(H_2C_2 - R)HC(H_2 -$ $(C - C)(e))$	$C_5$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	50.04	129.96	22.66	1.94462	0.49298
$R - H_2C_1C_2(H_2C_2 - R)HC(H_2 -$ $(C - C)(e))$	$C_6$	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	-17.08869	52.78	127.22	24.04	1.92443	0.47279
$R - H_2C_1C_2(H_2C_2 - R)HC(H_2 -$ $(C - C)(e))$	$C_7$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	50.04	129.96	22.66	1.94462	0.49298



Table 15.18. The energy parameters (eV) of functional groups of alkenes.

Parameters	C=C Group	C-C (i) Group	C-C (ii) Group	C-C (iii) Group	CH <sub>2</sub> (i) Group	CH <sub>3</sub> Group	CH <sub>2</sub> (ii) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$n_1$	2	1	1	1	2	3	2	1	1	1	1	1	1	1
$n_2$	0	0	0	0	1	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1
$c_1$	1	1	1	1	1	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$c_2$	0.91771	0.91771	0.91771	0.91771	0.91771	-0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$c_3$	0	1	0	1	1	0	1	1	0	0	0	1	1	0
$c_4$	4	2	2	2	1	1	1	1	2	2	2	2	2	2
$c_5$	0	0	0	0	2	3	2	1	0	0	0	0	0	0
$C_{10}$	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{10}$	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1
$V_e$ (eV)	-102.08992	-30.19634	-30.19634	-30.19634	-72.03287	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_f$ (eV)	21.48386	9.50874	9.50874	9.50874	26.02344	38.92728	25.78002	12.87680	9.33552	9.33552	9.37273	9.33552	9.37273	9.37273
$T$ (eV)	34.67062	7.37432	7.37432	7.37432	21.95990	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m$ (eV)	-17.33531	-3.68716	-3.68716	-3.68716	-10.97995	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{(10100)}$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{11,100}$ (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$E_{(10100)}$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{(11,10)}$ (eV)	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{(atom - atom, msp, AO)}$ (eV)	-2.26759	-1.44915	-1.85836	-1.44915	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{(101)}$ (eV)	-65.53833	-33.08452	-33.49373	-33.08452	-49.66493	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ (10 <sup>15</sup> rad/s)	43.0680	9.97851	16.4962	9.97851	25.2077	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_c$ (eV)	28.34813	6.58803	10.85807	6.58803	16.59214	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_n$ (eV)	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{K\alpha}$ (eV)	0.17897	0.15895	0.09931	0.09931	0.35532	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
	[6]	[7]	[8]	[8]	Eq. (13.458)	Eq. (13.458)	Eq. (13.458)	Eq. (13.458)	[2]	[4]	[5]	[2]	[2]	[2]
$\bar{E}_{\text{vac}}$ (eV)	-0.25568	-0.08827	-0.16869	-0.11809	-0.07727	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{\text{ring}}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{(10100)}$ (eV)	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{\text{ring}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{ring}}$ (eV)	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_p$ (eV)	7.51014	3.75498	4.39264	3.78480	7.83968	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734



Table 15.19. The total bond energies of alkenes calculated using the functional group composition and the energies of Table 15.18 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{\sigma}(\text{group})$  ( $\text{eV}$ ) values based on composition is given by (15.58).

Formula	Name	$C=C$	$C-C$ (i)	$C-C$ (ii)	$C-C$ (iii)	$CH_2$ (i)	$CH_3$	$CH_2$ (ii)	$CH$	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	$E_{mag}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_3H_6$	Propene	0	0	0	0	1	1	0	1	0	0	0	0	0	0	0	35.56033	35.63207	0.00201
$C_4H_8$	1-Butene	1	0	0	0	1	1	1	1	1	0	0	0	0	0	0	47.78477	47.78477	0.00140
$C_4H_8$	trans-2-Butene	1	0	2	0	0	2	0	2	0	0	0	0	0	0	0	47.90395	47.90395	-0.00057
$C_4H_8$	Isobutene	1	0	0	2	1	2	0	0	0	0	0	0	0	0	0	47.96096	47.96096	0.00121
$C_5H_{10}$	1-Pentene	1	0	1	0	1	1	2	1	0	0	0	0	0	0	0	59.87573	59.87573	0.00125
$C_5H_{10}$	trans-2-Pentene	1	0	0	0	2	1	1	2	1	0	0	0	0	0	0	60.08886	60.08886	-0.00043
$C_5H_{10}$	2-Methyl-1-butene	1	0	2	0	1	2	1	1	0	0	0	0	0	0	0	60.06084	60.09707	0.00060
$C_5H_{10}$	2-Methyl-2-butene	1	1	0	0	0	3	0	1	0	0	0	0	0	0	0	60.21435	60.16444	-0.00083
$C_5H_{10}$	3-Methyl-1-butene	1	0	1	0	1	3	0	2	0	2	0	0	0	0	0	59.97662	60.01727	0.00068
$C_6H_{12}$	1-Hexene	1	0	1	0	1	1	3	1	3	0	0	0	0	0	0	72.03343	72.12954	0.00133
$C_6H_{12}$	trans-2-Hexene	1	0	2	0	0	2	2	2	2	0	0	0	0	0	0	72.24656	72.23733	-0.00013
$C_6H_{12}$	trans-3-Hexene	1	0	0	2	1	2	2	2	2	0	0	0	0	0	0	72.24656	72.24251	-0.00006
$C_6H_{12}$	trans-4-Hexene	1	0	2	0	1	2	2	2	2	0	0	0	0	0	0	72.21854	72.29453	0.00105
$C_6H_{12}$	2-Methyl-1-pentene	1	0	0	2	1	1	1	1	1	2	0	0	0	0	0	72.37203	72.37206	0.00000
$C_6H_{12}$	2-Methyl-2-pentene	1	2	1	0	0	3	1	1	1	2	0	0	0	0	0	72.13432	72.19173	0.00080
$C_6H_{12}$	3-Methyl-1-pentene	1	0	1	0	1	2	1	2	1	3	0	0	0	0	0	72.10599	72.21038	0.00145
$C_6H_{12}$	4-Methyl-1-pentene	1	0	1	0	1	2	1	2	0	3	0	0	0	0	0	72.37203	72.33268	-0.00054
$C_6H_{12}$	3-Methyl-trans-2-pentene	1	2	1	0	0	3	1	1	1	0	0	0	0	0	0	72.37203	72.33268	-0.00054
$C_6H_{12}$	4-Methyl-trans-2-pentene	1	0	2	0	0	3	0	3	0	2	0	0	0	0	0	72.34745	72.31610	-0.00043
$C_6H_{12}$	pentene	1	0	2	0	0	3	0	3	0	2	0	0	0	0	0	72.21854	72.25909	0.00056
$C_7H_{14}$	2-Ethyl-1-butene	1	0	0	2	1	2	2	0	4	0	0	0	0	0	0	72.31943	72.32543	0.00008
$C_7H_{14}$	2,3-Dimethyl-1-butene	1	0	0	2	1	3	0	1	0	2	0	0	0	0	0	72.31796	72.30366	-0.00020
$C_7H_{14}$	3,3-Dimethyl-1-butene	1	0	1	0	1	0	0	1	0	0	3	0	0	-1	0	72.49750	72.38450	-0.00156
$C_7H_{14}$	2,3-Dimethyl-2-butene	1	4	0	0	0	4	0	0	0	0	0	0	0	0	0	84.19113	84.27084	0.00095
$C_7H_{14}$	1-Heptene	1	0	0	0	1	1	4	1	4	0	0	0	0	0	0	84.26369	84.30608	0.00050
$C_7H_{14}$	5-Methyl-1-hexene	1	0	1	0	1	2	2	2	1	3	0	0	0	0	0	84.52973	84.42112	-0.00129
$C_7H_{14}$	trans-3-Methyl-3-hexene	1	2	1	0	0	3	2	1	2	0	0	0	0	0	0	84.44880	84.49567	0.00053
$C_7H_{14}$	2,4-Dimethyl-1-pentene	1	0	0	2	1	3	1	1	0	3	0	0	0	0	0	84.27012	84.47087	0.00238
$C_7H_{14}$	4,4-Dimethyl-1-pentene	1	0	1	0	1	3	1	1	0	0	4	0	0	0	0	84.63062	84.54445	-0.00102
$C_7H_{14}$	2,4-Dimethyl-2-pentene	1	2	1	0	0	4	0	2	0	2	0	0	0	0	0	84.63062	84.54445	-0.00102
$C_7H_{14}$	trans-4,4-Dimethyl-2-pentene	1	0	2	0	0	4	0	2	0	0	3	0	0	-2	0	84.54076	84.54549	0.00006
$C_7H_{14}$	pentene	1	0	2	0	0	4	0	2	0	2	0	0	0	0	0	84.47713	84.44910	-0.00033
$C_7H_{14}$	2-Ethyl-3-methyl-1-butene	1	0	0	2	1	3	1	1	1	2	0	0	0	0	0	84.51274	84.51129	-0.00002
$C_7H_{14}$	2,3,3-Trimethyl-1-butene	1	0	0	2	1	4	0	0	0	0	3	0	0	-2	0	96.34883	96.41421	0.00068
$C_7H_{14}$	butene	1	0	0	1	1	5	1	1	5	0	0	0	0	0	0	96.69846	96.68782	-0.00011
$C_7H_{14}$	1-Octene	1	0	0	1	0	4	1	2	1	0	3	0	0	-2	0	96.63483	96.61113	-0.00025
$C_7H_{14}$	trans-2,2-Dimethyl-3-hexene	1	0	2	0	0	4	1	2	2	2	0	0	0	0	0	96.61293	96.71684	0.00107
$C_8H_{16}$	3-Ethyl-2-methyl-1-pentene	1	0	0	2	1	3	2	1	2	2	0	0	0	0	0	96.67590	96.65880	-0.00018
$C_8H_{16}$	2,4,4-Trimethyl-1-pentene	1	0	0	2	1	4	1	0	0	0	4	0	0	0	-3	120.74240	120.74240	0.00065
$C_8H_{16}$	2,4,4-Trimethyl-2-pentene	0	2	1	0	0	5	0	1	0	0	3	0	0	0	0	120.66423	145.07163	0.00063
$C_8H_{16}$	pentene	1	0	1	0	1	1	7	1	7	0	0	0	0	0	0	144.97963	145.07163	0.00063
$C_8H_{16}$	1-Decene	1	0	1	0	1	1	9	1	9	0	9	0	0	0	0	193.61043	193.71766	0.00055
$C_8H_{16}$	1-Dodecene	1	0	1	0	1	1	13	1	13	0	0	0	0	0	0	193.61043	193.71766	0.00055
$C_8H_{16}$	1-Hexadecene	1	0	1	0	1	1	13	1	13	0	0	0	0	0	0	193.61043	193.71766	0.00055



Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of  $\theta_e$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ .

[illegible]



# ALKYNES ( $C_nH_{2n-2}$ , $n = 3, 4, 5, \dots, \infty$ )

The straight and branched-chain alkynes,  $C_nH_{2n-2}$ , have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen atoms of acetylene. Based on the energy matching of the mutually bound  $C$ , these  $C-C$ -bond MOs are defined as primary and secondary  $C-C$  functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal  $CH$  of a primary alkyne comprises a functional group that is solved equivalently to the methylene group of acetylene as given in the Acetylene Molecule section.

10 The alkyl portion of the alkyne may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In 15 addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the  $2s$  and  $2p$  20 AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom,msp^3.AO)$  of the  $C \equiv C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is equivalent to that of acetylene,  $-3.13026 eV$ , given by Eq. (14.342).  $E_r(atom-atom,msp^3.AO)$  of each -alkyl-bond MO in 25 Eq. (15.52) is  $-1.85836 eV$  or  $-1.44915 eV$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 eV$  (Eq. (14.513)), or methyl,  $-0.72457 eV$  (Eq. (14.151)), groups, respectively. For the  $C-C$  groups each comprising a  $C$  single bond to  $C \equiv C$ ,  $E_r(atom-atom,msp^3.AO)$  is  $-0.72457 eV$  based on the energy match between the  $C2sp^3$  HOs for the mutually bound  $C$  of 30 the single and triple bonds. The parameter  $\omega$  of each group is matched for oscillation in the transition state based on the group being primary or secondary.



The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the  
5 sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.79-15.108) are given in Table 15.26. Each  $C$  of the  $C \equiv C$  group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene.



Table 15.21. The symbols of functional groups of alkynes.

Functional Group	Group Symbol
CC triple bond	$C \equiv C$
C single bond to $C \equiv C$ (1°)	C'-C' (i)
C single bond to $C \equiv C$ (2°)	C'-C' (ii)
CH (terminal)	C'-H (i)
$CH_2$ group	C'-H (CH <sub>2</sub> )
$CH_3$ group	C'-H (CH <sub>3</sub> )
CH (alkyl)	C'-H (ii)
CC bond (n-C)	C'-C' (a)
CC bond (iso-C)	C'-C' (b)
CC bond (tert-C)	C'-C' (c)
CC (iso to iso-C)	C'-C' (d)
CC (t to t-C)	C'-C' (e)
CC (t to iso-C)	C'-C' (f)

Table 15.22. The geometrical bond parameters of alkynes and experimental values [1].

Parameter	$C \equiv C$ Group	C'-C' (i) Group	C'-C' (ii) Group	C'-H (i) Group	C'-H (CH <sub>2</sub> ) Group	C'-H (CH <sub>3</sub> ) Group	C'-H (ii) Group	C'-C' (a) Group	C'-C' (b) Group	C'-C' (c) Group	C'-C' (d) Group	C'-C' (e) Group	C'-C' (f) Group
$a$ (Å)	1.28714	1.99185	1.99185	1.48719	1.67122	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.13452	1.41133	1.41133	0.99572	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.20072	1.49369	1.49369	1.05383	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.203 (acetylene) 1.208 (2,4-hexadiyne)	1.450 (2,4-hexadiyne)	1.450 (2,4-hexadiyne)	1.060 (acetylene)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c$ (Å)	0.60793	1.40557	1.40557	1.10466	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.88143	0.70855	0.70855	0.66953	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.23. The MO to HO intercept geometrical bond parameters of alkynes.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{nspp}, \text{AO})$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{final}}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$R-C \equiv C-H$	C <sub>u</sub>	-1.5613	0	0	0	-153.18082	0.83008	-16.39088	-16.20002	90.99	89.01	48.71	0.98144	0.01428
$C-C \equiv C-H$	C <sub>u</sub>	-1.5613	-0.30229	0	0	-153.54311	0.81213	-16.75317	-16.56231	137.17	42.83	65.25	0.53890	0.59562
$C-C \equiv C-H$	C <sub>u</sub>	-1.5613	0	0	0	-153.18082	0.83008	-16.39088	-16.20002	137.91	42.09	66.24	0.51853	0.61599
$C-C \equiv C-H$	C <sub>u</sub>	-0.30229	-0.92918	0	0	-152.90716	0.84418	-16.11722	-15.92636	75.71	104.29	35.59	1.61974	0.20841
$C-H (CH_3)$	C <sub>u</sub>	-0.92918	0	0	0	-152.44487	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H (CH_3)$	C <sub>u</sub>	-0.92918	-0.92918	0	0	-153.47406	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H (CH)$	C <sub>u</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_1C-C_1H_2CH_2-$ (C-C (a))	C <sub>u</sub>	-0.92918	0	0	0	-152.54487	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_1C-C_1H_2CH_2-$ (C-C (a))	C <sub>u</sub>	-0.92918	-0.92918	0	0	-153.47406	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_1C-C_1(H_2C-R)HCH_2-$ (C-C (b))	C <sub>u</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_1C-C_1(R'-H_1C)C_1(R''-H_1C)CH_2-$ (C-C (c))	C <sub>u</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	-17.92866	-17.73779	48.21	131.79	21.74	1.97374	0.50570
$HO-C_1C_1(H_2C-R)HCH_2-$ (C-C (d))	C <sub>u</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$HO-C_1(R'-H_1C)C_1(R''-H_1C)CH_2-$ (C-C (e))	C <sub>u</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$HO-C_1C_1(H_2C-R)HCH_2-$ (C-C (f))	C <sub>u</sub>	-0.72457	-0.92918	-0.92918	0	-154.19663	0.91771	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$HO-C_1(R'-H_1C)C_1(R''-H_1C)CH_2-$ (C-C (f))	C <sub>u</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.24. The energy parameters (eV) of functional groups of alkyne.

Parameters	C $\equiv$ C Group	C-C (i) Group	C-C (ii) Group	C-H (i) Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H (ii) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$n_1$	3	1	1	1	3	2	1	1	1	1	1	1	1
$n_2$	0	0	0	0	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	2	1	1	0	0	1	1	0	0	0	1	1	0
$C_6$	6	2	2	1	1	1	1	2	2	2	2	2	2
$C_7$	0	0	0	1	3	2	1	0	0	0	0	0	0
$C_{10}$	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{20}$	1	1	1	1	1	1	1	1	1	1	1	1	1
$V_r$ (eV)	-182.53826	-31.29307	-31.29307	-40.62396	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-29.10112
$V_r$ (eV)	35.97770	9.64042	9.64042	13.66428	38.92728	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.37273
$T$ (eV)	70.90876	7.85528	7.85528	13.65796	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m$ (eV)	-35.45438	-3.92764	-3.92764	-6.82898	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{(atom)}$ (eV)	-16.20002	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{(atom)}$ (eV)	0	-0.72457	-0.72457	-3.13026	0	0	0	0	0	0	0	0	0
$E_{(atom)}$ (eV)	-16.20002	-13.91032	-13.91032	-11.50462	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{(atom)}$ (eV)	-94.90616	-31.63533	-31.63533	-31.63532	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T$ (atom - atom, msp, AO) (eV)	-3.13026	-0.72457	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T$ (eV)	-98.03637	-32.35994	-32.35994	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ (10 <sup>5</sup> rad/s)	20.0186	10.3988	17.5426	30.8370	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K$ (eV)	13.17659	6.84470	11.54682	20.29747	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_D$ (eV)	-0.23468	-0.16749	-0.21754	-0.28197	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{K_{max}}$ (eV)	0.27773	0.08989	0.08989	0.35532	0.35532	0.35532	0.35532	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
$E_{K_{max}}$ (eV)	-0.09581	-0.12255	-0.17260	-0.10430	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{K_{max}}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{(atom)}$ (eV)	-98.02775	-32.48249	-32.53254	-31.73967	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{(atom)}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{(atom)}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{(atom)}$ (eV)	10.21841	3.21271	3.26276	3.50634	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734







# ALKYL FLUORIDES ( $C_nH_{2n+2-m}F_m$ , $n=1,2,3,4,5\ldots\infty$ $m=1,2,3\ldots\infty$ )

The branched-chain alkyl fluorides,  $C_nH_{2n+2-m}F_m$ , may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds wherein at least one  $H$  is replaced by a fluorine. The  $C-F$  bond comprises a functional group for each case of  $F$  replacing a  $H$  of methane in the series  $H_{4-m}C-F_m$ ,  $m=1,2,3,4$ , and  $F$  replacing a  $H$  of an alkane. The methyl, methylene, methylene functional groups are equivalent to those of branched-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the  $C-F$  functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $F$  AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $F$  AO has an energy of  $E(F) = -17.42282 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-F$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-F$ -bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO \text{ to } F) = \frac{E(C, 2sp^3)}{E(F)} c_2(C2sp^3HO) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}} (0.91771) = 0.77087 \quad (15.110)$$

$E_r(\text{atom-atom}, msp^3.AO)$  of the  $C-F$ -bond MO in Eq. (15.52) based on the charge donation from  $F$  to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the  $F$  atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl fluorides are



given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  (eV) values based on composition is given by Eq. (15.58). In the case of trifluoromethane,  $E_{mag}$  is positive since the term due to the fluorine atoms cancels that of the  $CH$  group. The  $C-C$  bonds to the  $CHF$  group (one  $H$  bond to  $C$ ) were each treated as an iso  $C-C$  bond. The  $C-C$  bonds to the  $CF$  group (no  $H$  bonds to  $C$ ) were each treated as a tert-butyl  $C-C$ .  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.110) are given in Table 15.32.

Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

Functional Group	Group Symbol
CF of $CF_m H_{4-m}$	$C-F$ (i)
CF of $C_n H_{2n+2-m} F_m$	$C-F$ (ii)
$CH_3$ group	$C-H$ ( $CH_3$ )
$CH_2$ group	$C-H$ ( $CH_2$ )
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)



Table 15.28. The geometrical bond parameters of branched-chain alkyl fluorides and experimental values [1].

Parameter	$C-F$ (i)	$C-F$ (ii)	$C-H$ ( $CH_3$ )	$C-H$ ( $CH_2$ )	$C-H$ Group	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)
$a$ ( $a_0$ )	1.72139	1.72139	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ ( $a_0$ )	1.31202	1.31202	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ( $\text{\AA}$ )	1.38858	1.38858	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ( $\text{\AA}$ )	1.382 (methyl fluoride)	1.382 (methyl fluoride)	1.107 ( $C-H$ propane)	1.107 ( $C-H$ propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
$h_{C'}$ ( $a_0$ )	1.11435	1.11435	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.76219	0.76219	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.29. The MO to HO intercept geometrical bond parameters of branched-chain alkyl fluorides.  $R, R', R''$  are H or alkyl groups.  $E_{\sigma}$  is  $E_{\sigma}(atom - atom, mvp^2, AO)$ .

Bond	Atom	$E_{\sigma}$ (eV) Bond 1	$E_{\sigma}$ (eV) Bond 2	$E_{\sigma}$ (eV) Bond 3	$E_{\sigma}$ (eV) Bond 4	Final Total Energy ( $C2sp^3$ ) (eV)	$r_{final}$ ( $a_0$ )	$r_{final}$ ( $a_0$ )	$E_{\sigma}(eV)$ Final	$E(C2sp^3)$ (eV) Final	$\theta'$ ( $^{\circ}$ )	$\theta_1$ ( $^{\circ}$ )	$\theta_2$ ( $^{\circ}$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$H_{4+u}C_{-u}^+-F_{-u}^-$ ( $C^+-F$ (i))	$C_{-u}$	-1.34946	0	0	0	-152.96515	0.91771	0.84115	-16.17521	-15.98435	100.77	79.23	47.86	1.15488	0.15714
$H_{4+u}C_{-u}^+-F_{-u}^-$ ( $C^+-F$ (ii))	$F$	-1.34946	0	0	0	-153.89433	0.78069	0.84115	-16.17521	-16.91353	100.77	79.23	47.86	1.15488	0.15714
$-H_2C_2^+C_2^-F$ ( $C^+-F$ (iii))	$C_{-u}$	-1.34946	-0.92918	0	0	-153.89433	0.91771	0.79546	-17.10440	-16.91353	97.02	82.98	45.11	1.21483	0.09718
$-H_2C_2^+C_2^-F$ ( $C^+-F$ (iv))	$F$	-1.34946	0	0	0	-154.40324	0.78069	0.84115	-16.17521	-17.42244	100.77	79.23	47.86	1.15488	0.15714
$C^+-H$ ( $CH_2$ )	$C'$	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C^+-H$ ( $CH_2$ )	$C'$	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C^+-H$ ( $CH$ )	$C'$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.7326
$H_2C_2^+C_2^+H_2^-H_2^-$ ( $C^+-C$ (a))	$C_u$	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.33879	0.38106
$H_2C_2^+C_2^+H_2^-H_2^-$ ( $C^+-C$ (b))	$C_h$	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_2^+(H_2C_2^+-R')HC(H_2^-)$ ( $C^+-C$ (c))	$C_h$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2^+(R''-H_2C_2^+)C_2^-(R''-H_2C_2^+)CH_2^-$ ( $C^+-C$ (d))	$C_h$	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoHC_2^+(H_2C_2^+-R')HC(H_2^-)$ ( $C^+-C$ (e))	$C_h$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$isoHC_2^+(R''-H_2C_2^+)C_2^-(R''-H_2C_2^+)CH_2^-$ ( $C^+-C$ (f))	$C_h$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$isoHC_2^+(H_2C_2^+-R')HC(H_2^-)$ ( $C^+-C$ (g))	$C_h$	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoHC_2^+(R''-H_2C_2^+)C_2^-(R''-H_2C_2^+)CH_2^-$ ( $C^+-C$ (h))	$C_h$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.30. The energy parameters (eV) of functional groups of branched-chain alkyl fluorides.

Parameters	C-F (i)	C-F (ii)	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$n_1$	1	1	3	2	1	1	1	1	1	1	1
$n_2$	0	0	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.77087	0.77087	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	0	0	0	0	0	0	0	0	0
$C_6$	2	2	1	1	1	2	2	2	2	2	2
$C_7$	0	0	3	2	1	0	0	0	0	0	0
$C_{10}$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{10}$	1	1	1	1	1	1	1	1	1	1	1
$V_1$ (eV)	-32.02108	-32.02108	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_2$ (eV)	10.37015	10.37015	38.92728	25.78002	12.87680	9.3352	9.3352	9.37273	9.3352	9.37273	9.37273
$V_3$ (eV)	9.30097	9.30097	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_4$ (eV)	-4.65048	-4.65048	-16.26957	-10.53337	-3.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{10}$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{10,100}$ (eV)	0	0	0	0	0	0	0	0	0	0	0
$E_{10}$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{10}$ (eV)	-31.63534	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{10}$ (eV)	-2.69802	-2.69802	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$\omega$ (10 <sup>5</sup> rad/s)	-34.33429	-34.33429	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$E_{10}$ (eV)	24.8506	24.8506	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{10}$ (eV)	16.35707	16.35707	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{10}$ (eV)	-0.27472	-0.27472	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{10}$ (eV)	0.13849	0.10911	0.35532	0.35532	0.35532	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
$E_{10}$ (eV)	-0.20547	-0.14371	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{10}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{10}$ (eV)	-34.53976	-34.47800	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{10}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{10}$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{10}$ (eV)	5.26998	5.20822	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.31. The total bond energies of branched-chain alkyl fluorides calculated using the functional group composition and the energies of Table 15.30 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{10}$  values based on composition is given by (15.58).

Formula	Name	C-F (i)	C-F (ii)	CH <sub>3</sub>	CH <sub>2</sub>	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	$E_{mag}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF <sub>4</sub>	Tetrafluoromethane	4	0	0	0	0	0	0	0	0	0	0	0	21.07992	21.016	-0.00303
CHF <sub>3</sub>	Trifluoromethane	3	0	0	0	1	0	0	0	0	0	0	1	19.28398	19.362	0.00405
CH <sub>2</sub> F <sub>2</sub>	Diffuoromethane	2	0	0	1	0	0	0	0	0	0	0	0	18.37012	18.280	-0.00496
C <sub>2</sub> H <sub>5</sub> F	1-Fluoropropane	0	1	1	2	0	0	0	0	0	0	0	-1	41.86745	41.885	0.00041
C <sub>3</sub> H <sub>7</sub> F	2-Fluoropropane	0	1	2	0	1	0	0	0	0	0	0	-1	41.96834	41.963	-0.00012







# ALKYL CHLORIDES ( $C_n H_{2n+2-m} Cl_m$ , $n=1,2,3,4,5\ldots\infty$ $m=1,2,3\ldots\infty$ )

The branched-chain alkyl chlorides,  $C_n H_{2n+2-m} Cl_m$ , may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds wherein at least one  $H$  is replaced by a chlorine. The  $C-Cl$  bond comprises a functional group for each case of  $Cl$  replacing a  $H$  of methane for the series  $H_{4-m}C-Cl_m$ ,  $m=1,2,3$ , with the  $C-Cl$  bond of  $CCl_4$  comprising another functional group due to the limitation of the minimum energy of  $Cl$  matched to that of the  $C2sp^3$  HO. In addition, the  $C-Cl$  bond due to  $Cl$  replacing a  $H$  of an alkane is a function group. The methyl, methylene, methylene functional groups are equivalent to those of branched-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the  $C-Cl$  functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $Cl$  AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chlorine is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then,  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $Cl$  AO has an energy of  $E(Cl) = -12.96764 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-Cl$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the  $C-Cl$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } Cl) = \frac{E(Cl)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-12.96764 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.81317 \quad (15.110)$$

The valence energy of the carbon  $2p$  is  $-11.2603 \text{ eV}$  and that of the  $Cl$  AO is  $-12.96764 \text{ eV}$ .

The energy difference is more than that of  $2E_r(C-C, 2sp^3)$  given by Eq. (14.151) for a single



bond. Thus,  $E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C - Cl$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $Cl$  atoms to the MO is  $-1.44915 \text{ eV}$  based on the energy match between the  $C2sp^3$  HO and the  $Cl$  AO corresponding to the energy contributions equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)).

- 5 The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each
- 10  $E_D(\text{Group})$  of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The  $C - C$  bonds to the  $CHCl$  group (one  $H$  bond to  $C$ ) were each treated as an iso  $C - C$  bond. The  $C - C$  bonds to the  $CCl$  group (no  $H$  bonds to  $C$ ) were
- 15 each treated as a tert-butyl  $C - C$ .  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.38.

Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

Functional Group	Group Symbol
CCl of $CCl_m H_{4-m}$	$C - Cl$ (i)
CCl of $CCl_4$	$C - Cl$ (ii)
CCl of $C_n H_{2n+2-m} Cl_m$	$C - Cl$ (iii)
$CH_3$ group	$C - H$ ( $CH_3$ )
$CH_2$ group	$C - H$ ( $CH_2$ )
CH	$C - H$
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 15.34. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

Table 15.34. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

Parameter	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-Cl$ (iii) Group	$C-H$ ( $CH_3$ ) Group	$C-H$ ( $CH_2$ ) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$\alpha$ ( $a_n$ )	2.32621	2.37026	2.32621	1.64920	1.67122	1.67465	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ ( $a_n$ )	1.69136	1.70729	1.69136	1.04856	1.05553	1.05661	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ( $\text{\AA}$ )	1.79005	1.86692	1.79005	1.10974	1.11713	1.11827	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\text{\AA})$	1.785 (methyl chloride)	1.767 (carbon tetrachloride)	1.802 (ethyl chloride) 1.790 (1,2-dichloroethane)	1.107 ( $C-H$ propane) 1.117 ( $C-H$ butane)	1.107 ( $C-H$ propane) 1.117 ( $C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h_c$ ( $a_n$ )	1.59703	1.64416	1.59703	1.27295	1.29569	1.29924	1.54616	1.52750	1.54616	1.52750	1.52750
	0.72709	0.72030	0.72709	0.63380	0.63159	0.63095	0.63600	0.63888	0.63600	0.63888	0.63888

Table 15.35. The MO to HO intercept geometrical bond parameters of branched-chain alkyl chlorides.  $R, R', R''$  are H or alkyl groups.  $E_T = E_T(\text{atom} - \text{atom}, \text{msp}^3, AC)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy ( $^{2\text{exp}}$ ) (eV)	$r_{\text{initial}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{relaxation}}$ (eV) Final	$E(C_{2v}^{\text{exp}})$ Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$H_{1-2}C_1C_2-C^*H_m$ , $m=1,2,3$ ( $C^*-C1$ (ii))	$C^*$	-0.72457	0	0	0	-152.24026	0.91771	0.87495	-15.55033	-15.33946	69.62	110.38	30.90	1.99599	0.30463
$H_{1-2}C_1C_2-C^*H_m$ , $m=1,2,3$ ( $C^*-C1$ (ii))	$C^*$	-0.72457	0	0	0	-152.24026	1.05158	0.87495	-15.55033	-15.33946	69.62	110.38	30.90	1.99599	0.30463
$C^*C_1C_2$ ( $C^*-C1$ (iii))	$C^*$	-0.46459	0	0	0	-152.06028	0.91771	0.88983	-15.29034	-15.09948	66.98	115.02	29.87	2.05530	0.34801
$C^*C_1C_2$ ( $C^*-C1$ (iii))	$C^*$	-0.46459	0	0	0	-152.06028	1.05158	0.88983	-15.29034	-15.09948	66.98	115.02	29.87	2.05530	0.34801
$-H_1C_1C_2-C^*C_1$ ( $C^*-C1$ (iii))	$C^*$	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	63.18	116.82	27.48	2.66384	0.37248
$-H_1C_1C_2-C^*C_1$ ( $C^*-C1$ (iii))	$C^*$	-0.72457	-0.92918	0	0	-153.26945	1.05158	0.82562	-16.47951	-16.28864	63.18	116.82	27.48	2.66384	0.37248
$C^*-H_1C_1C_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C^*-H_1C_1C_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.20933
$C^*-H_1C_1C_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_1C_1C_2C_1C_2H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$H_1C_1C_2C_1C_2H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$R^*-H_1C_1C_2(H_1C_1C_2-C^*)HC^*H_2$ ( $C^*-C1$ (iii))	$C^*$	-0.92918	-0.92918												



Table 15.36. The energy parameters (eV) of functional groups of branched-chain alkyl chlorides.

Parameters	C-Cl (i) Group	C-Cl (ii) Group	C-Cl (iii) Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	1	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0	0
$\zeta_1$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_2$	0.81317	0.81317	0.81317	1	1	1	1	1	1	1	1	1
$\zeta_3$	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\zeta_4$	1	1	1	0	1	1	0	0	0	1	1	0
$\zeta_5$	2	2	2	1	1	1	2	2	2	2	2	2
$\zeta_6$	0	0	0	3	2	1	0	0	0	0	0	0
$\zeta_{10}$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_{20}$	0.81317	0.81317	0.81317	1	1	1	1	1	1	1	1	1
$\nu_1$ (eV)	-29.68411	-28.95265	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$\nu_2$ (eV)	8.04432	7.96922	8.04432	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$\nu_3$ (eV)	6.38036	6.10748	6.38036	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$\nu_4$ (eV)	-3.19018	-3.05374	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$\nu_5$ (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.55946	-15.56407	-15.55946	-15.55946
$\Delta E_{1,2}^{(1,2)}$ (eV)	-1.44915	-0.92918	-1.44915	0	0	0	0	0	0	0	0	0
$\nu_7$ (eV)	-13.18574	-13.70571	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.55946	-15.56407	-15.55946	-15.55946
$\nu_8$ (eV)	-31.63536	-31.63540	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63533	-31.63537	-31.63533	-31.63533
$\nu_9$ (eV)	-1.44915	-0.92918	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$\nu_{10}$ (eV)	-33.08452	-32.56455	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^{15}$ rad/s)	7.42995	7.22380	13.0612	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_1$ (eV)	4.89052	4.75483	8.59708	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_2$ (eV)	-0.14475	-0.14048	-0.19191	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_3$ (eV)	0.08059	0.08059	0.09113	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_4$ (eV)	-0.10445	-0.10019	-0.14635	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{100}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{100}^{(100)}$ (eV)	-33.18897	-32.66473	-33.23086	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24376	-33.59732	-33.18712	-33.18712
$E_{100}^{(100,100)}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{100}^{(100,100,100)}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$F_{10}$ (eV)	3.77116	3.39496	3.96108	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734



Table 15.37. The total bond energies of branched-chain alkyl chlorides calculated using the functional group composition and the energies of Table 15.36 compared to the experimental values [2]. The magnetic energy  $E_{ms}$  that is subtracted from the weighted sum of the  $E_{\sigma}(E_{\text{lower}})$  ( $eV$ ) values based on composition is given by (15.58).

Formula	Name	C-Cl (i)	C-Cl (ii)	C-Cl (iii)	CH <sub>3</sub>	CH <sub>2</sub>	CH (i)	CH (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	$E_{ms}$	Calculated Total Bond Energy (eV)	Experiment al Total Bond Energy (eV)	Relative Error
CCl <sub>4</sub>	Tetrachloromethane	0	0	4	0	0	0	0	0	0	0	0	0	0	-1	13.43181	13.448	0.00123
CHCl <sub>3</sub>	Trichloromethane	3	0	0	0	0	1	0	0	0	0	0	0	0	-1	14.49146	14.523	0.00217
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane	2	0	0	0	1	0	0	0	0	0	0	0	0	0	15.37248	15.450	0.00499
CH <sub>3</sub> Cl	Chloromethane	1	0	0	1	0	0	0	0	0	0	0	0	0	0	16.26302	16.312	0.00299
C <sub>2</sub> H <sub>5</sub> Cl	1-Chloroethane	0	0	1	1	1	0	0	0	1	0	0	0	0	0	28.61064	28.571	-0.00138
C <sub>3</sub> H <sub>7</sub> Cl	1-Chloropropane	0	0	1	1	2	0	0	2	0	0	0	0	0	0	40.76834	40.723	-0.00112
C <sub>4</sub> H <sub>9</sub> Cl	1-Chlorobutane	0	0	1	2	3	0	1	0	2	0	0	0	0	0	40.86923	40.858	-0.00028
C <sub>5</sub> H <sub>11</sub> Cl	1-Chloropentane	0	0	1	2	3	0	1	3	0	0	0	0	0	0	52.92604	52.903	-0.00044
C <sub>6</sub> H <sub>13</sub> Cl	1-Chlorohexane	0	0	1	2	3	0	1	3	0	0	0	0	0	0	52.02693	52.972	-0.00104
C <sub>7</sub> H <sub>15</sub> Cl	1-Chloro-2-methylpropane	0	0	1	2	3	0	1	3	0	0	0	0	0	0	52.99860	52.953	-0.00085
C <sub>8</sub> H <sub>17</sub> Cl	1-Chloro-2-methylbutane	0	0	1	3	4	0	0	0	3	0	0	0	0	-1	53.21057	53.191	-0.00037
C <sub>9</sub> H <sub>19</sub> Cl	1-Chloro-3-methylbutane	0	0	1	3	4	0	0	4	0	0	0	0	0	0	65.08379	65.061	0.00034
C <sub>10</sub> H <sub>21</sub> Cl	2-Chloro-2-methylbutane	0	0	1	2	2	1	0	3	0	0	0	0	0	0	65.15630	65.111	-0.00069
C <sub>11</sub> H <sub>23</sub> Cl	2-Chloro-3-methylbutane	0	0	1	3	3	1	0	1	0	0	0	0	0	-1	65.36827	65.344	-0.00037
C <sub>12</sub> H <sub>25</sub> Cl	2-Chlorohexane	0	0	1	3	0	2	0	3	0	3	1	0	0	0	65.16582	65.167	0.00002
C <sub>13</sub> H <sub>27</sub> Cl	1-Chlorooctane	0	0	1	2	3	1	0	3	2	0	0	0	0	0	77.34233	77.313	-0.00038
C <sub>14</sub> H <sub>29</sub> Cl	1-Chlorodecane	0	0	1	1	7	0	0	7	0	0	0	0	0	0	101.55684	101.564	0.00007
C <sub>15</sub> H <sub>31</sub> Cl	1-Chlorododecane	0	0	1	1	11	0	0	11	0	0	0	0	0	0	150.87640	150.202	0.00009
C <sub>16</sub> H <sub>33</sub> Cl	1-Chlorotetradecane	0	0	1	1	7	0	0	7	0	0	0	0	0	0	223.13384	223.175	0.00018



Table 15.38. The bond angle parameters of branched-chain alkyl chlorides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

Atom of angle	$2c_1$ Bond 1 ( $a_1$ )	$2c_2$ Bond 2 ( $a_2$ )	$2c_3$ Terminal Atom ( $a_3$ )	$E_{\text{terminal}}$ Atom 1 (Table 15.3.A)	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{terminal}}$ Atom 2 (Table 15.3.A)	Atom 2 Hybridization Designation (Table 15.3.A)	$c_1$ Atom 1	$c_2$ Atom 2	$c_3$	$C_1$	$C_2$	$C_3$	$E_i$ (eV)	$\theta_i$ ( $^\circ$ )	$\theta_i$ ( $^\circ$ )	$\theta_i$ ( $^\circ$ )	Cal. $\theta_i$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))	3.36271	3.36271	5.3689	-14.82575 $C_1$	I	-14.82575 $C_1$	I	0.91771	0.91771	I	0.81317 (Eq. (15.11))			-0.92918				111.40	112.0 (dichloromethane)
$\angle \text{H}_1\text{C}_1\text{C}_2$ ( $C_2 - C_1$ (iii))	2.11106	3.36271	4.5961	-16.27499 $C_2$	IS	-12.96764 $C_1$	CI	0.83600	0.91771	0.75	0.9310 (Eq. (15.63))			0				111.46	
$\angle \text{H}_1\text{C}_1\text{H}_2$ ( $C_2 - C_1$ (iii))	2.09711	2.09711	3.4252	-15.75493 $C_2$	II		II	0.86359	I	0.75	I			0				109.50	109.2 (2-chloropropane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))															70.56			109.44	109.8 (2-chloropropane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))	2.91547	3.36271	5.1539	-15.75493 $C_2$	7	-12.96764 $C_1$	CI	0.86359	0.86359	I	0.81317 (Eq. (15.11))			-0.92918				109.61	110.6 (ethyl chloride)
$\angle \text{C}_1\text{C}_2\text{H}_3$ ( $C_2 - C_1$ (iii))	2.91547	2.11106	4.1633	-15.59033 $C_2$	5	-14.82575 $C_1$	I	0.87495	0.91771	0.75	I			0				110.83	110.6 (ethyl chloride)
$\angle \text{H}_1\text{C}_1\text{H}_2$ ( $C_2 - C_1$ (iii))	2.11106	2.11106	3.4252	-15.75493 $C_2$	7	II	II	0.86359	I	0.75	I			0				108.44	107 (propane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))															69.51			110.49	112 (propane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))															69.51			110.49	113.8 (butane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))															70.56			109.44	110.8 (butane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))															70.56			109.44	111.0 (butane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))	2.91547	2.91547	4.7958	-16.04412 $C_2$	25	-16.04412 $C_1$	25	0.81549	0.81549	I	I			-1.83836				110.67	110.8 (hexane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))	2.91547	2.11325	4.1633	-15.59033 $C_2$	5	-14.82575 $C_1$	I	0.87495	0.91771	0.75	I			0				110.76	
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))	2.91547	2.09711	4.1633	-15.59033 $C_2$	5	-14.82575 $C_1$	I	0.87495	0.91771	0.75	I			0				111.27	111.4 (heptane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))	2.90327	2.90327	4.7958	-15.59033 $C_2$	5	-14.82575 $C_1$	I	0.87495	0.91771	0.75	I			-1.83836				111.27	111.4 (heptane)
$\angle \text{C}_1\text{C}_2\text{C}_3$ ( $C_2 - C_1$ (iii))															72.50			107.50	



# ALKYL BROMIDES ( $C_n H_{2n+2-m} Br_m$ , $n=1,2,3,4,5\ldots\infty$ $m=1,2,3\ldots\infty$ )

The branched-chain alkyl bromides,  $C_n H_{2n+2-m} Br_m$ , may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds wherein at least one  $H$  is replaced by a bromine. The  $C-Br$  bond comprises a functional group for each case of  $Br$  replacing a  $H$  of methane for the series  $H_{4-m} C-Br_m$ ,  $m=1,2,3$ , with the  $C-Br$  bond of  $CBr_4$  comprising another functional group due to the limitation of the minimum energy of  $Br$  matched to that of the  $C2sp^3$  HO. In addition, the  $C-Br$  bond due to  $Br$  replacing a  $H$  of an alkane is a function group. The methyl, methylene, methylene functional groups are equivalent to those of branched-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the  $C-Br$  functional groups comprises the hybridization of the  $2s$  and  $2p$  shells of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  hybridized orbital (HO) and the  $Br$  AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $Br$  AO has an energy of  $E(Br) = -11.81381 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-Br$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the  $C-Br$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3 HO \text{ to } Br) = \frac{E(Br)}{E(C, 2sp^3)} c_2(C2sp^3 HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.74081 \quad (15.112)$$



The valence energy of the carbon  $2p$  is  $-11.2603 \text{ eV}$  and that of the  $Br$  AO is  $-11.81381 \text{ eV}$ . The energy difference is less than that of  $E_r(C-C, 2sp^3)$  given by Eq. (14.151) for a single bond. Thus,  $E_r(atom - atom, msp^3.AO)$  of the alkyl  $C-Br$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $Br$  atoms to the MO is  $-0.92918 \text{ eV}$  (Eq. (14.513) based on the maximum single-bond-energy contribution of the  $C2sp^3$  HO.  $E_r(atom - atom, msp^3.AO)$  of the series  $CBr_m H_{4-m}$ ,  $m=1,2,3$  is equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)). For  $CBr_4$ ,  $E_r(atom - atom, msp^3.AO)$  of the  $C-Br$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $Br$  atoms to the MO is  $-0.36229 \text{ eV}$  (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of  $s=1$ ,  $E_r(atom - atom, msp^3.AO) = -0.72457 \text{ eV}$  and  $E_r(atom - atom, msp^3.AO) = 0$ ) based on the maximum charge density on the  $C2sp^3$  HO.

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl bromides are given in Tables 15.40, 15.41, and 15.42, respectively. The total energy of each branched-chain alkyl bromide given in Table 15.43 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.42 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(Group)$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The  $C-C$  bonds to the  $CHBr$  group (one  $H$  bond to  $C$ ) were each treated as an iso  $C-C$  bond. The  $C-C$  bonds to the  $CBr$  group (no  $H$  bonds to  $C$ ) were each treated as a tert-butyl  $C-C$ .  $E_{mag}$  is subtracted for each t-butyl group. In the case of 2,3-dibromo-2-methylbutane,  $E_{mag}$  is positive since the terms due to the two bromine atoms cancel that of the t-butyl and  $CH$  groups. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.112) are given in Table 15.44.



Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

Functional Group	Group Symbol
CBr of $CB_r_m H_{4-m}$	$C - Br$ (i)
CBr of $CB_r_4$	$C - Br$ (ii)
CBr of $C_n H_{2n+2-m} Br_m$	$C - Br$ (iii)
$CH_3$ group	$C - H$ ( $CH_3$ )
$CH_2$ group	$C - H$ ( $CH_2$ )
CH	$C - H$
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 15.40. The geometrical bond parameters of branched-chain alkyl bromides and experimental values [1].

Parameter	C-Br (i)	C-Br (ii)	C-Br (iii)	C-H (CH <sub>3</sub> )	C-H (CH <sub>2</sub> )	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
$\alpha$ (°)	2.49163	2.52309	2.47329	1.67122	1.64920	1.67465	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (°)	1.83395	1.84622	1.82719	1.04856	1.04856	1.05661	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (Å)	1.94097	1.95396	1.95381	1.10974	1.10974	1.11713	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.953 (methyl bromide)	1.955 (carbon tetrabromide)	1.93 (1,1,1-tribromoethane)	1.107 (C-H propane)	1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane)	1.531 (butane)	1.532 (propane)	1.531 (butane)	1.532 (propane)
$h_c$ (°)	1.68667	1.72265	1.66689	1.27295	1.27295	1.29569	1.54616	1.52750	1.54616	1.52750	1.52750
$\epsilon$	0.73604	0.73115	0.73877	0.63580	0.63580	0.63159	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.41. The MO to HO intercept geometrical bond parameters of branched-chain alkyl bromides.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^2, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy (2sp <sup>2</sup> ) (eV)	$r_{\text{final}}$ (a <sub>0</sub> )	$r_{\text{final}}$ (a <sub>0</sub> )	$E_{\text{redox}}$ (eV) Final	$E(2sp^2)$ (eV) Final	$\theta'$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
$H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$	C	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	68.10	111.90	29.52	2.16808	0.33415
$H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$	Br	-0.36229	0	0	0	-151.97798	1.15169	0.89582	-15.18804	-14.99717	68.10	111.90	29.52	2.16808	0.33415
$(C_{\text{atom}} - Br_{\text{atom}})$ (i)	C	-0.18114	0	0	0	-151.79683	0.91771	0.90664	-15.00689	-14.81063	66.10	113.90	28.76	2.21357	0.36734
$(C_{\text{atom}} - Br_{\text{atom}})$ (ii)	Br	-0.18114	0	0	0	-151.79683	1.15169	0.90664	-15.00689	-14.81063	66.10	113.90	28.76	2.21357	0.36734
$(C_{\text{atom}} - Br_{\text{atom}})$ (iii)	C	-0.46459	-0.92918	0	0	-153.09546	0.91771	0.83885	-16.21952	-16.02866	62.67	117.33	26.55	2.21237	0.36518
$(C_{\text{atom}} - Br_{\text{atom}})$ (iv)	Br	-0.46459	-0.92918	0	0	-153.09546	1.15169	0.83885	-16.21952	-16.02866	62.67	117.33	26.55	2.21237	0.36518
$(C_{\text{atom}} - H_{\text{atom}})$ (i)	C	-0.92918	0	0	0	-152.44487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$(C_{\text{atom}} - H_{\text{atom}})$ (ii)	Br	-0.92918	0	0	0	-152.44487	1.15169	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$(C_{\text{atom}} - H_{\text{atom}})$ (iii)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29953
$(C_{\text{atom}} - H_{\text{atom}})$ (iv)	Br	-0.92918	-0.92918	0	0	-153.47406	1.15169	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29953
$(C_{\text{atom}} - H_{\text{atom}})$ (v)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61350	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$(C_{\text{atom}} - H_{\text{atom}})$ (vi)	Br	-0.92918	-0.92918	-0.92918	0	-154.40324	1.15169	0.77247	-17.61350	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$(C_{\text{atom}} - H_{\text{atom}})$ (vii)	C	-0.92918	0	0	0	-153.44487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.35486	0.29953
$(C_{\text{atom}} - H_{\text{atom}})$ (viii)	Br	-0.92918	0	0	0	-153.44487	1.15169	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.35486	0.29953
$(C_{\text{atom}} - H_{\text{atom}})$ (ix)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$(C_{\text{atom}} - H_{\text{atom}})$ (x)	Br	-0.92918	-0.92918	0	0	-153.47406	1.15169	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$(C_{\text{atom}} - H_{\text{atom}})$ (xi)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61350	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(C_{\text{atom}} - H_{\text{atom}})$ (xii)	Br	-0.92918	-0.92918	-0.92918	0	-154.40324	1.15169	0.77247	-17.61350	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(C_{\text{atom}} - H_{\text{atom}})$ (xiii)	C	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95754	0.50570
$(C_{\text{atom}} - H_{\text{atom}})$ (xiv)	Br	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	1.15169	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95754	0.50570
$(C_{\text{atom}} - H_{\text{atom}})$ (xv)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61350	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(C_{\text{atom}} - H_{\text{atom}})$ (xvi)	Br	-0.92918	-0.92918	-0.92918	0	-154.40324	1.15169	0.77247	-17.61350	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(C_{\text{atom}} - H_{\text{atom}})$ (xvii)	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.41399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$(C_{\text{atom}} - H_{\text{atom}})$ (xviii)	Br	-0.72457	-0.72457	-0.72457	-0.72457	-154.41399	1.15169	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$(C_{\text{atom}} - H_{\text{atom}})$ (xix)	C	-0.72457	-0.72457	-0.92918	0	-154.9863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$(C_{\text{atom}} - H_{\text{atom}})$ (xx)	Br	-0.72457	-0.72457	-0.92918	0	-154.9863	1.15169	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$(C_{\text{atom}} - H_{\text{atom}})$ (xxi)	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.41399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$(C_{\text{atom}} - H_{\text{atom}})$ (xxii)	Br	-0.72457	-0.72457	-0.72457	-0.72457	-154.41399	1.15169	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.42. The energy parameters (eV) of functional groups of branched-chain alkyl bromides.

Table 13.42. The energy parameters (eV) of functional groups of branched-chain alkyl boundaries.											
Parameters	C-Br (i) Group	C-Br (ii) Group	C-Br (iii) Group	CH <sub>3</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	1	1	3	2	1	1	1	1	1	1
$\eta_2$	0	0	0	2	1	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5
$C_2$	0.74081	0.74081	0.74081	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1
$C_4$	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	0	0	1	0	0	0	1	1	0
$C_6$	2	2	2	1	1	2	2	2	2	2	2
$C_7$	0	0	0	3	2	1	0	0	0	0	0
$C_8$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5
$C_{in}$	0.74081	0.74081	0.74081	1	1	1	1	1	1	1	1
$C_{out}$	-27.94806	-27.44996	-28.22940	-107.32728	-70.41425	-35.12015	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_1$ (eV)	7.41885	7.36955	7.44631	38.92728	25.78002	12.87680	9.33552	9.37273	9.33552	9.37273	9.37273
$V_2$ (eV)	5.60839	5.43544	5.70686	32.53914	21.06675	10.48582	6.77464	6.90500	6.77464	6.90500	6.90500
$V_3$ (eV)	-2.80419	-2.71772	-2.85443	-16.26957	-10.53337	-5.24291	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{L(in)}^L$ (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{L(in)}^L$ (eV)	-0.72457	-0.36229	-0.92918	0	0	0	0	0	0	0	0
$E_{L(in)}^L$ (eV)	-13.91032	-14.27260	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{L(in)}^L$ (eV)	-31.63553	-31.63557	-31.63557	-67.69451	-49.66493	-31.63553	-31.63557	-31.63553	-31.63557	-31.63553	-31.63553
$E_{L(in)}^L$ (eV)	-0.72457	-0.36229	-0.92918	0	0	0	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{L(in)}^L$ (eV)	-32.35994	-31.99766	-32.56455	-67.69450	-49.66493	-31.63557	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^{16}$ rad/s)	6.39733	6.27059	6.46864	24.9386	24.2751	24.1759	9.43699	15.4846	9.43699	15.4846	9.55643
$E_{\Sigma}$ (eV)	4.21083	4.12741	4.25777	16.40846	15.97831	15.91299	6.21159	10.19220	6.21159	10.19220	6.29021
$\bar{E}_{\Sigma}$ (eV)	-0.13137	-0.12861	-0.13293	-0.25552	-0.25017	-0.24966	-0.16515	-0.20896	-0.16515	-0.20896	-0.16416
$\bar{E}_{\Sigma}^{(e)}$ (eV)	0.07575	0.08332	0.07575	0.35532	0.35532	0.35532	0.17978	0.09944	0.12312	0.12312	0.12312
$\bar{E}_{\Sigma}^{(e)}$ (eV)	-0.09349	-0.08695	-0.09506	-0.22757	-0.14502	-0.07200	-0.10359	-0.15924	-0.10359	-0.15924	-0.10260
$E_{\Sigma}^{(e)}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\Sigma}^{(e)}$ (eV)	-32.45343	-32.08460	-32.65961	-67.92207	-49.80996	-31.70737	-33.59732	-33.24576	-33.59732	-33.18712	-33.18712
$E_{\Sigma}^{(e)}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\Sigma}^{(e)}$ (eV)	0	0	0	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\Sigma}^{(e)}$ (eV)	3.18365	2.81482	3.38983	12.49186	7.83016	3.32601	4.32754	4.29921	4.17951	3.62128	3.91754







# ALKYL IODIDES ( $C_n H_{2n+2-m} I_m$ , $n=1,2,3,4,5\ldots\infty$ $m=1,2,3\ldots\infty$ )

The branched-chain alkyl iodides,  $C_n H_{2n+2-m} I_m$ , may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds wherein at least one  $H$  is replaced by an iodine atom. The  $C-I$  bond comprises a functional group for  $I$  replacing a  $H$  of methane ( $CH_3I$ ) or for  $I$  replacing a  $H$  of an alkane corresponding to the series  $C_n H_{2n+2-m} I_m$ . The  $C-I$  bond of each of  $CH_2I_2$  and  $CHI_3$  comprise separate functional groups due to the limitation of the minimum energy of  $I$  matched to that of the  $C2sp^3$  HO. The methyl, methylene, methylene functional groups are equivalent to those of branched-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the  $C-I$  functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $I$  AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)). The  $I$  AO has an energy of  $E(I) = -10.45126 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-I$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.51) for the  $C-I$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } I) = \frac{E(I)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.45126 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.65537 \quad (15.113)$$

The valence energy of the carbon  $2p$  is  $-11.2603 \text{ eV}$  and that of the  $I$  AO is  $-10.45126 \text{ eV}$ .

The energy difference is positive. Thus, based on the maximum charge density on the  $C2sp^3$



HO  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$  of the  $C - I$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $I$  atoms to the MO is  $-0.36229 \text{ eV}$  (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of  $s=1$ ,  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO}) = -0.72457 \text{ eV}$  and  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO}) = 0$ ) for methyl and alkyl iodides,  $-0.18114 \text{ eV}$  for diiodomethane, 5 and 0 for  $\text{CHI}_3$ .

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl iodides are given in Tables 15.46, 15.47, and 15.48, respectively. The total energy of each branched-chain 10 alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{\text{mag}}$  that was subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The  $C - C$  bonds to the  $\text{CHI}$  group (one  $H$  bond to  $C$ ) were each 15 treated as an iso  $C - C$  bond. The  $C - C$  bonds to the  $\text{CI}$  group (no  $H$  bonds to  $C$ ) were each treated as a tert-butyl  $C - C$ .  $E_{\text{mag}}$  is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.113) are given in Table 15.50.

20 Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

Functional Group	Group Symbol
CI of $\text{CH}_3\text{I}$ and $\text{C}_n\text{H}_{2n+2-m}\text{I}_m$	$C - I$ (i)
CI of $\text{CH}_2\text{I}_2$	$C - I$ (ii)
CI of $\text{CHI}_3$	$C - I$ (iii)
$\text{CH}_3$ group	$C - H$ ( $\text{CH}_3$ )
$\text{CH}_2$ group	$C - H$ ( $\text{CH}_2$ )
CH	$C - H$
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 15.46. The geometrical bond parameters of branched-chain alkyl iodides and experimental values [1].

Parameter	C-I (i) Group	C-I (ii) Group	C-I (iii) Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H (CH) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\sigma$ (Å)	2.67103	2.68865	2.70662	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	2.01881	2.02546	2.03222	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (Å)	2.13662	2.14365	2.15081	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	2.132 (methyl iodide)	2.132 (methyl iodide)	2.15 (carbon tetrachloride)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c$ (Å)	1.74894	1.76815	1.78770	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.75582	0.75334	0.75083	0.63380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.47. The MO to HO intercept geometrical bond parameters of branched-chain alkyl iodides.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \Delta O)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C_{2sp^3}$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{ioniz}}$ (eV) Final	$E(C_{2sp^3})$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C^*H_3I$ ( $C_0-I$ (i))	$C^*$	-0.18114	0	0	0	-151.79683	0.91771	0.90664	-15.00689	-14.81603	69.63	110.37	29.08	2.33442	0.31560
$C^*H_3I$ ( $C_0-I$ (ii))	$I$	-0.18114	0	0	0		1.30183	0.90664	-15.00689		69.63	110.37	29.08	2.33442	0.31560
$-H_3C^*C^*I$ ( $C_0-I$ (i))	$C^*$	-0.18114	-0.92918	0	0	-152.72602	0.91771	0.83377	-15.93608	-15.74521	63.16	116.84	25.82	2.40456	0.38554
$-H_3C^*C^*I$ ( $C_0-I$ (ii))	$I$	-0.18114	0	0	0		1.30183	0.90664	-15.00689		69.63	110.37	29.08	2.33442	0.31560
$C^*H_3I_2$ ( $C_0-I$ (iii))	$C^*$	-0.09057	0	0	0	-151.70626	0.91771	0.91214	-14.91632	-14.72546	68.61	111.39	28.71	2.35818	0.33272
$C^*H_3I_2$ ( $C_0-I$ (iv))	$I$	-0.09057	0	0	0		1.30183	0.91214	-14.91632		68.61	111.39	28.71	2.35818	0.33272
$C_0HI_3$ ( $C_0-I$ (iii))	$C_0$	0	0	0	0	-151.61569	0.91771	0.91771	-14.82575	-14.63489	67.56	112.44	28.32	2.38256	0.35055
$C_0HI_3$ ( $C_0-I$ (iv))	$I$	0	0	0	0		1.30183	0.91771	-14.82575	-14.63489	67.56	112.44	28.32	2.38256	0.35055
$C^*H_3(C^*H_3)$ ( $C_0-H$ (i))	$C^*$	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	71.49	100.51	41.48	1.23564	0.18708
$C^*H_3(C^*H_3)$ ( $C_0-H$ (ii))	$C^*$	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29953
$C^*H_3(C^*H_3)$ ( $C_0-H$ (iii))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.7247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37356
$H_3C^*C^*H_3(C^*H_3)$ ( $C-C$ (a))	$C^*$	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C^*C^*H_3(C^*H_3)$ ( $C-C$ (b))	$C^*$	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	125.59	26.06	1.90890	0.45117
$R-H_3C^*C^*(H_3C^*C^*-R')H_3C^*H_2-$ ( $C-C$ (c))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.7247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_3C^*C^*(H_3C^*C^*-R')H_3C^*H_2-$ ( $C-C$ (d))	$C^*$	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$terC^*(H_3C^*C^*-R')H_3C^*H_2-$ ( $C-C$ (e))	$C^*$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.7247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$terC^*(H_3C^*C^*-R')H_3C^*H_2-$ ( $C-C$ (f))	$C^*$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51999	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$terC^*(H_3C^*C^*-R')H_3C^*H_2-$ ( $C-C$ (g))	$C^*$	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$terC^*(H_3C^*C^*-R')H_3C^*H_2-$ ( $C-C$ (h))	$C^*$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51999	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.48. The energy parameters (eV) of functional groups of branched-chain alkyl iodides.

Parameters	C-I (i)	C-I (ii)	C-I (iii)	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	C-C (f) Group
$\eta_1$	1	1	1	3	2	1	1	1	1	1	1	1	1
$\eta_2$	0	0	0	2	1	0	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	0.65537	0.65537	0.65537	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	1	0	1	0	1	1	0	0	0	1	1	1	0
$C_6$	2	2	2	1	1	1	2	2	2	2	2	2	2
$C_7$	0	0	0	3	2	1	0	0	0	0	0	0	0
$C_{10}$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$C_{11}$	0.65537	0.65537	0.65537	1	1	1	1	1	1	1	1	1	1
$C_{12}$	-26.59109	-26.34902	-26.10696	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112	-29.10112
$V_e$ (eV)	6.75951	6.71739	6.69505	38.92728	25.78002	12.87680	9.3352	9.3352	9.37273	9.3352	9.37273	9.37273	9.37273
$T$ (eV)	4.97768	4.82280	4.82280	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500	6.90500
$V_{\text{ion}}$ (eV)	-2.48884	-2.45002	-2.41140	-16.20957	-10.53357	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250	-3.45250
$E_{\text{ion}}$ (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{\text{ion}}$ (eV)	-0.36229	-0.18114	0	0	0	0	0	0	0	0	0	0	0
$E_{\text{ion}}$ (eV)	-14.29907	-14.45375	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{\text{ion}}$ (eV)	-31.63554	-31.63555	-31.63554	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63533	-31.63537	-31.63533	-31.63533	-31.63533
$E_{\text{ion}}$ (eV)	-0.36229	-0.18114	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915	-1.44915
$E_{\text{ion}}$ (eV)	-31.99766	-31.81651	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452	-33.08452
$\omega$ (10 <sup>11</sup> rad/s)	10.2318	5.36799	9.90080	24.2751	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	15.4846	9.55643	9.55643
$E_{\text{ion}}$ (eV)	6.73472	3.53331	6.51688	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	10.19220	6.29021	6.29021
$E_{\text{ion}}$ (eV)	-0.16428	-0.11832	-0.15977	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.20896	-0.16416	-0.16416
$E_{\text{ion}}$ (eV)	0.06608	0.06608	0.06608	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.09944	0.12312	0.12312
$E_{\text{ion}}$ (eV)	-0.13124	-0.08527	-0.12673	-0.22757	-0.14502	-0.07200	-0.10359	-0.0726	-0.15924	-0.10359	-0.15924	-0.10260	-0.10260
$E_{\text{ion}}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\text{ion}}$ (eV)	-32.12889	-31.90179	-31.76210	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24576	-33.59732	-33.24576	-33.18712	-33.18712
$E_{\text{ion}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{ion}}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0	0
$E_{\text{ion}}$ (eV)	2.71108	2.63201	2.34429	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734	3.91734

Table 15.49. The total bond energies of branched-chain alkyl iodides calculated using the functional group composition and the energies of Table 15.48 compared to the experimental values [2]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_{\text{p}}(\text{group})$  (eV) val based on composition is given by (15.58).

Name	C-I (i)	C-I (ii)	C-I (iii)	CH <sub>3</sub>	CH <sub>2</sub>	CH (i)	CH (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	$E_{\text{mag}}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
Tridimethylmethane	0	0	3	0	0	1	0	0	0	0	0	0	0	0	10.5588	10.05	0.0444
Dimethylmethane	0	2	0	0	1	0	0	0	0	0	0	0	0	-1	12.94614	12.921	-0.00095
Iodomethane	1	0	0	1	0	0	0	0	0	0	0	0	0	0	15.20294	15.163	-0.00263
Iodoethane	1	0	0	1	1	0	0	0	0	0	0	0	0	0	22.56064	22.543	-0.00066
1-Iodopropane	1	0	0	1	2	0	0	2	0	0	0	0	0	0	30.51834	30.516	-0.00006
2-Iodopropane	1	0	0	2	0	1	0	0	2	0	0	0	0	0	30.61903	30.633	0.00069
2-Iodo-2-methylpropane	1	0	0	3	0	0	0	0	0	0	0	0	0	-1	51.96057	51.999	-0.00119



Table 15.50. The bond angle parameters of branched-chain alkyl iodides and experimental values [1]. In the calculation of  $\theta_p$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, nsp^2, AO)$ .

Atom 1 Angle	$2c_1'$ ( $\theta_1$ )	$2c_2'$ ( $\theta_2$ )	$2c_3'$ ( $\theta_3$ )	$F_{\text{valence}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$F_{\text{valence}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$\zeta$	$E_T$ (eV)	$\theta_p$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C-I-I$ ( $C-I-I$ )	4.0392	4.0392	6.7205	-10.45126 $I$	1	-10.45126 $I$	1	1	1	1	0.6537 (Eq. (15.113))	1	1	-0.30228				112.10	
$\angle HC-I$ ( $C-I-I$ )	2.1106	4.03763	5.2203	-14.82575 $C'$	1	-10.45126 $I$	1	0.91771	0.91771	0.75	0.76815 (Eq. (15.63))	0.75	1.00000	0				112.39	
$\angle HC-H$ ( $C-I-I$ )	2.09711	2.09711	3.4252	-15.75493 $C''$	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	111.2 (methyl iodide)
$\angle C'-C'-H$ ( $C'-I-I$ )																70.56		109.44	
$\angle C-C-I$ ( $C'-I-I$ )	2.91547	4.03763	5.7939	-15.55033 $C'$	5	-10.45126 $I$	1	0.87495	0.87495	1	0.6537 (Eq. (15.113))	1	0.7495	-0.36228				111.86	
$\angle HC-H$ ( $C-I-I$ )	2.1106	2.1106	3.4252	-15.75493 $C''$	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C'-C'-C$																		110.49	112 (propane) 115.8 (butane) 110.8 (isobutane) 111.0 (butane) 111.4 (isobutane)
$\angle C'-C-H$																		110.49	
$\angle HC-H$	2.09711	2.09711	3.4252	-15.75493 $C''$	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C'-C'-C$																		109.44	
$\angle C'-C-H$																		109.44	
$\angle C'-C'-C$																		110.67	110.8 (isobutane)
$\angle C'-C-H$	2.91547	2.91547	4.7938	-16.68412 $C'$	25	-16.68412 $C'$	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.76	
$\angle C'-C-H$	2.91547	2.11223	4.1633	-15.55033 $C''$	5	-14.82575 $C'$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C'-C-H$	2.91547	2.09711	4.1633	-15.55033 $C''$	5	-14.82575 $C'$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C'-C'-C$	2.90327	2.90327	4.7938	-15.55033 $C''$	5	-14.82575 $C'$	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C'-C'-C$																72.50		107.50	



# ALKENYL HALIDES ( $C_n H_{2n-m} X_m$ , $n = 3, 4, 5 \dots \infty$ $m = 1, 2, 3 \dots \infty$ )

The branched-chain alkenyl halides,  $C_n H_{2n+2-m} X_m$  with  $X = F, Cl, Br, I$ , may comprise alkyl and alkenyl functional groups wherein at least one  $H$  is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl  $H$ , the  $C-X$  bond comprises the alkyl-halogen functional groups given in their respective sections. The alkenyl halogen  $C-X$  bond comprises a separate functional group for each case of  $X$  bonding to the  $C=C$ -bond functional group given in the Alkenes section. In addition the  $CH$  group of the moiety  $XCH=C$  comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes,  $C_n H_{2n}$ , comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are  $C$  vinyl single bond to  $-C(C)=C$ ,  $C$  vinyl single bond to  $-C(H)=C$ , and  $C$  vinyl single bond to  $-C(C)=CH_2$ . In addition,  $CH_2$  of the  $-C=CH_2$  moiety is also an alkene functional group solved in the Alkenes section.

Consider the case where  $X = Cl$  substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct  $C-Cl$  functional groups can be identified:  $Cl$  vinyl single bond to  $-C(C)=C$  and  $Cl$  vinyl single bond to  $-C(H)=C$ . The alkenyl-halide  $CH$  group is equivalent to that solved in the Hydrogen Carbide ( $CH$ ) section except that  $\Delta E_{H_2MO}(AO/HO) = -1.13379 \text{ eV}$  in order to energy match to the  $C-Cl$  and  $C=C$  bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.



$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C = C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is equivalent to that of ethylene,  $-2.26759 \text{ eV}$ , given by Eq. (14.247).  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of each  $C - C$ -bond MO in Eq. (15.52) is  $-1.85836 \text{ eV}$  or  $-1.44915 \text{ eV}$  based on the energy match between the  $C2sp^3$  HOs  
 5 corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 \text{ eV}$  (Eq. (14.513), or methyl,  $-0.72457 \text{ eV}$  (Eq. (14.151)), groups, respectively.

The solution of each  $C - X$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $X$  AO to form a MO permits each participating  
 10 orbital to decrease in radius and energy. The alkenyl  $C - X$ -bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the  $C - X$ -bond MO are each energy matched to the alkene  $C2sp^3$  HO. In alkenyl halides with  $X = Cl, Br, \text{ or } I$ , the energy of the halogen atom is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq.  
 15 (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. For example, the hybridization factor  $C_2$  of Eq. (15.52) for the alkenyl  $C - Cl$ -bond MO given by Eq. (15.111) is  $C_2(C2sp^3HO \text{ to } Cl) = 0.81317$ .

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the alkenyl  $C - Cl$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $Cl$  atoms to the MO is  $-0.72457 \text{ eV}$  for the  $Cl$  vinyl single  
 20 bond to  $-C(H) = C - Cl$  group and  $-0.92918 \text{ eV}$  for the  $Cl$  vinyl single bond to  $-C(C) = C - Cl$  group. It is based on the energy match between the  $Cl$  atom and the  $C2sp^3$  HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in  
 25 Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.54 corresponding to functional-group composition of the molecule.



The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.56.

Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

Functional Group	Group Symbol
Cl vinyl single bond to -C(H)=C	$C - Cl$ (i)
Cl vinyl single bond to -C(C)=C	$C - Cl$ (ii)
CC double bond	$C = C$
C vinyl single bond to -C(C)=C	$C - C$ (i)
C vinyl single bond to -C(H)=C	$C - C$ (ii)
C vinyl single bond to -C(C))=CH <sub>2</sub>	$C - C$ (iii)
CH (alkenyl halide)	$C - H$ (i)
CH <sub>2</sub> alkenyl group	$C - H$ (CH <sub>2</sub> ) (i)
CH <sub>3</sub> group	$C - H$ (CH <sub>3</sub> )
CH <sub>2</sub> alkyl group	$C - H$ (CH <sub>2</sub> ) (ii)
CH (alkyl)	$C - H$ (ii)
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 1.5.52. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

Parameter	C-Cl (i) Group	C-Cl (ii) Group	C-Cl (iii) Group	C-H (i) Group	C-H (ii) Group	C-H (iii) Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>3</sub> ) Group	C-H (i) Group	C-H (ii) Group	C-H (iii) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\sigma$ (Å)	2.15818	2.19338	1.47228	2.04740	2.04740	2.04740	1.64010	1.60061	1.64920	1.67122	1.67465	2.12499	2.12499	2.12499	2.10725	2.10725	2.10725	2.10725
$\sigma^+$ (Å)	1.62912	1.64243	1.26661	1.43087	1.43087	1.43087	1.04566	1.03299	1.04856	1.05553	1.05661	1.45744	1.45744	1.45744	1.45164	1.45164	1.45164	1.45164
Bond Length $2\sigma^+$ (Å)	1.72419	1.73827	1.34032	1.51437	1.51437	1.51437	1.10668	1.09327	1.10974	1.11713	1.11827	1.54280	1.54280	1.54280	1.53635	1.53635	1.53635	1.53635
Exp. Bond Length (Å)	1.730 (vinyl chloride) 1.73 (1,1-dichloroethylene)	1.730 (vinyl chloride) 1.73 (1,1-dichloroethylene)	1.342 (2-methylpropane) 1.346 (2-butene) 1.349 (1,3-butadiene)	1.508 (2-butene)	1.508 (2-methylpropane)	1.508 (2-methylpropane)	1.10 (2-methylpropane) 1.108 (1,3-butadiene)	1.09 (vinyl chloride)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, \sigma$ (Å)	1.41552	1.45403	0.75055	1.46439	1.46439	1.46439	1.26354	1.22665	1.27295	1.29569	1.29924	1.54616	1.54616	1.54616	1.52750	1.52750	1.52750	1.52750
$\sigma$	0.75486	0.74874	0.86030	0.69887	0.69887	0.69887	0.63756	0.64537	0.63580	0.63159	0.63095	0.68600	0.68600	0.68600	0.68888	0.68888	0.68888	0.68888



Table 15.53. The MO to HO intercept geometrical bond parameters of branched-chain alkyl chlorides.  $R, R', R''$  are H or alkyl groups.  $E_p$  is  $E_p(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

Bond	Atom	$E_p$ (eV) Bond 1	$E_p$ (eV) Bond 2	$E_p$ (eV) Bond 3	$E_p$ (eV) Bond 4	Final Total Energy (eV)	$r_{\text{bond}}$ (Å)	$r_{\text{bond}}$ (Å)	$E_p(2sp^3)$ (eV) Final	$\theta^*$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (Å)	$d_2$ (Å)
$C_1 = C_1(C) - H(CH)$	$C_1$	-1.34946	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	76.99	103.01	40.53	1.21653	0.18354
$-C_8 = C_1(H)C_1$ (C-C) (i)	$C_8$	-1.13379	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	79.43	100.57	34.49	1.77872	0.14960
$-C_8 = C_1(H)C_1$ (C-C) (ii)	$C_1$	-0.72457	0	0	0		1.05158	0.87495	-15.50533	85.36	94.64	38.03	1.69955	0.07083
$-C_8 = C_1(C)C_1$ (C-C) (i)	$C_8$	1.13379	-0.46459	-0.92918	0	-154.14326	0.91771	0.78405	-17.53532	72.17	107.83	30.88	1.88253	0.24010
$-C_8 = C_1(C)C_1$ (C-C) (ii)	$C_1$	-0.46459	0	0	0		1.05158	0.88983	-15.25034	83.62	96.38	37.46	1.74125	0.09882
$C_1(H)C_1 = C_1H_2C_2$	$C_1$	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	127.61	52.39	38.24	0.77492	0.49168
$C_1(H)C_1 = C_1H_2C_2$	$C_8$	-1.13380	0	0	0	-152.74949	0.91771	0.82552	-15.95955	129.84	50.16	60.70	0.72040	0.54620
$C_2(C)C_1 = C_1H_2C_2$	$C_2$	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	126.39	53.61	56.95	0.80289	0.46371
$R_1C_1H_2 - C_1(C) = C$ (C-C) (i)	$C_1$	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	60.88	119.12	27.79	1.81127	0.38039
$R_1C_1H_2 - C_1(C) = C$ (C-C) (ii)	$C_8$	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	67.40	112.60	31.36	1.74821	0.31754
$R_1C_1H_2 - C_1(H) = C$ (C-C) (i)	$C_8$	-1.13380	-0.92918	0	0	-153.67866	0.91771	0.80561	-16.88873	64.57	115.43	22.79	1.77684	0.34595
$R_1C_1H_2 - C_1(H) = C$ (C-C) (ii)	$C_1$	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	65.99	114.01	30.38	1.76270	0.33185
$C - H(CH_2)$	$C$	-1.13380	0	0	0	-152.74949	0.91771	0.82552	-15.95955	77.15	102.85	41.13	1.23331	0.18965
$C - H(CH_2)$	$C$	-0.92918	0	0	0	-152.54487	0.91771	0.86559	-15.75493	71.49	102.51	41.48	1.23564	0.18708
$C - H(CH_2)$	$C$	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	68.47	111.53	35.84	1.35466	0.29933
$C - H(CH_2)$	$C$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.41330	61.10	118.90	31.37	1.42088	0.37326
$H_1C_1C_2H_2CH_2 -$ (C-C) (i)	$C_1$	-0.92918	0	0	0	-152.54487	0.91771	0.86559	-15.75493	63.82	116.18	30.08	1.83879	0.38106
$H_1C_1C_2H_2CH_2 -$ (C-C) (ii)	$C_8$	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	56.41	123.59	26.06	1.90890	0.45117
$R - H_1C_1C_2(H_1C_2 - R)HCCH_2 -$ (C-C) (i)	$C_8$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.41330	48.30	131.70	21.90	1.97162	0.51388
$R - H_1C_1C_2(H_1C_2 - R)HCCH_2 -$ (C-C) (ii)	$C_1$	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.52866	48.21	131.79	21.74	1.95734	0.50570
$R_1C_1C_2H_2CH_2 - R$ (C-C) (i)	$C_8$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.41330	48.30	131.70	21.90	1.97162	0.51388
$R_1C_1C_2H_2CH_2 - R$ (C-C) (ii)	$C_1$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.52866	50.04	129.96	22.66	1.94462	0.49298
$R_1C_1C_2H_2CH_2 - R$ (C-C) (i)	$C_8$	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	52.78	127.22	24.04	1.92443	0.47279
$R_1C_1C_2H_2CH_2 - R$ (C-C) (ii)	$C_1$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.52866	50.04	129.96	22.66	1.94462	0.49298



Table 15.54 The energy parameters (eV) of functional groups of branched-chain alkenyl chlorides.

[illegible]

T-41a, 15.55. The total bond energies of branched-chain alkene chlorides calculated using the functional group composition and the energies of Table 15.54 compared to the experimental values [21].

Table 15.55. The bond energies of branched-chain alkyl chlorides calculated using the functional group composition and the energies of Table 15.54 compared to the experimental values [2].

Formula	Name	C—C bond energies compared to the experimental values [2]										Experimental Total Bond Energy (kJ/mol)	Relative Error		
		C—Cl (f)	C—Cl (g)	C—C (f)	C—C (g)	C—C (iii)	C—C (ii)	C—C (i)	CH <sub>2</sub> (i)	CH <sub>3</sub> (ii)	CH <sub>3</sub> (iii)				
C <sub>3</sub> H <sub>7</sub> Cl	Chloroethane	1	0	1	0	0	1	1	0	0	0	0	0	22,595	0.00170
C <sub>4</sub> H <sub>9</sub> Cl	2-Chloropropane	0	1	1	0	0	1	1	0	0	0	0	0	33,029.84	0.00071



Table 15.56. The bond angle parameters of branched-chain alkeryl chlorides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_i$  is  $E_i \left( atom, nsp^i, AO \right)$ .

Atom of Angle	$2c_1^*$ Bond 1 ( $a_1$ )	$2c_2^*$ Bond 2 ( $a_2$ )	$2c_3^*$ Central Atom ( $a_3$ )	$F_{\text{center}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$F_{\text{center}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}$	$c_{13}$	$c_{14}$	$c_{15}$	$c_{16}$	$c_{17}$	$c_{18}$	$c_{19}$	$c_{20}$	$c_{21}$	$c_{22}$	$c_{23}$	$c_{24}$	$c_{25}$	$c_{26}$	$c_{27}$	$c_{28}$	$c_{29}$	$c_{30}$	$c_{31}$	$c_{32}$	$c_{33}$	$c_{34}$	$c_{35}$	$c_{36}$	$c_{37}$	$c_{38}$	$c_{39}$	$c_{40}$	$c_{41}$	$c_{42}$	$c_{43}$	$c_{44}$	$c_{45}$	$c_{46}$	$c_{47}$	$c_{48}$	$c_{49}$	$c_{50}$	$c_{51}$	$c_{52}$	$c_{53}$	$c_{54}$	$c_{55}$	$c_{56}$	$c_{57}$	$c_{58}$	$c_{59}$	$c_{60}$	$c_{61}$	$c_{62}$	$c_{63}$	$c_{64}$	$c_{65}$	$c_{66}$	$c_{67}$	$c_{68}$	$c_{69}$	$c_{70}$	$c_{71}$	$c_{72}$	$c_{73}$	$c_{74}$	$c_{75}$	$c_{76}$	$c_{77}$	$c_{78}$	$c_{79}$	$c_{80}$	$c_{81}$	$c_{82}$	$c_{83}$	$c_{84}$	$c_{85}$	$c_{86}$	$c_{87}$	$c_{88}$	$c_{89}$	$c_{90}$	$c_{91}$	$c_{92}$	$c_{93}$	$c_{94}$	$c_{95}$	$c_{96}$	$c_{97}$	$c_{98}$	$c_{99}$	$c_{100}$	$c_{101}$	$c_{102}$	$c_{103}$	$c_{104}$	$c_{105}$	$c_{106}$	$c_{107}$	$c_{108}$	$c_{109}$	$c_{110}$	$c_{111}$	$c_{112}$	$c_{113}$	$c_{114}$	$c_{115}$	$c_{116}$	$c_{117}$	$c_{118}$	$c_{119}$	$c_{120}$	$c_{121}$	$c_{122}$	$c_{123}$	$c_{124}$	$c_{125}$	$c_{126}$	$c_{127}$	$c_{128}$	$c_{129}$	$c_{130}$	$c_{131}$	$c_{132}$	$c_{133}$	$c_{134}$	$c_{135}$	$c_{136}$	$c_{137}$	$c_{138}$	$c_{139}$	$c_{140}$	$c_{141}$	$c_{142}$	$c_{143}$	$c_{144}$	$c_{145}$	$c_{146}$	$c_{147}$	$c_{148}$	$c_{149}$	$c_{150}$	$c_{151}$	$c_{152}$	$c_{153}$	$c_{154}$	$c_{155}$	$c_{156}$	$c_{157}$	$c_{158}$	$c_{159}$	$c_{160}$	$c_{161}$	$c_{162}$	$c_{163}$	$c_{164}$	$c_{165}$	$c_{166}$	$c_{167}$	$c_{168}$	$c_{169}$	$c_{170}$	$c_{171}$	$c_{172}$	$c_{173}$	$c_{174}$	$c_{175}$	$c_{176}$	$c_{177}$	$c_{178}$	$c_{179}$	$c_{180}$	$c_{181}$	$c_{182}$	$c_{183}$	$c_{184}$	$c_{185}$	$c_{186}$	$c_{187}$	$c_{188}$	$c_{189}$	$c_{190}$	$c_{191}$	$c_{192}$	$c_{193}$	$c_{194}$	$c_{195}$	$c_{196}$	$c_{197}$	$c_{198}$	$c_{199}$	$c_{200}$	$c_{201}$	$c_{202}$	$c_{203}$	$c_{204}$	$c_{205}$	$c_{206}$	$c_{207}$	$c_{208}$	$c_{209}$	$c_{210}$	$c_{211}$	$c_{212}$	$c_{213}$	$c_{214}$	$c_{215}$	$c_{216}$	$c_{217}$	$c_{218}$	$c_{219}$	$c_{220}$	$c_{221}$	$c_{222}$	$c_{223}$	$c_{224}$	$c_{225}$	$c_{226}$	$c_{227}$	$c_{228}$	$c_{229}$	$c_{230}$	$c_{231}$	$c_{232}$	$c_{233}$	$c_{234}$	$c_{235}$	$c_{236}$	$c_{237}$	$c_{238}$	$c_{239}$	$c_{240}$	$c_{241}$	$c_{242}$	$c_{243}$	$c_{244}$	$c_{245}$	$c_{246}$	$c_{247}$	$c_{248}$	$c_{249}$	$c_{250}$	$c_{251}$	$c_{252}$	$c_{253}$	$c_{254}$	$c_{255}$	$c_{256}$	$c_{257}$	$c_{258}$	$c_{259}$	$c_{260}$	$c_{261}$	$c_{262}$	$c_{263}$	$c_{264}$	$c_{265}$	$c_{266}$	$c_{267}$	$c_{268}$	$c_{269}$	$c_{270}$	$c_{271}$	$c_{272}$	$c_{273}$	$c_{274}$	$c_{275}$	$c_{276}$	$c_{277}$	$c_{278}$	$c_{279}$	$c_{280}$	$c_{281}$	$c_{282}$	$c_{283}$	$c_{284}$	$c_{285}$	$c_{286}$	$c_{287}$	$c_{288}$	$c_{289}$	$c_{290}$	$c_{291}$	$c_{292}$	$c_{293}$	$c_{294}$	$c_{295}$	$c_{296}$	$c_{297}$	$c_{298}$	$c_{299}$	$c_{300}$	$c_{301}$	$c_{302}$	$c_{303}$	$c_{304}$	$c_{305}$	$c_{306}$	$c_{307}$	$c_{308}$	$c_{309}$	$c_{310}$	$c_{311}$	$c_{312}$	$c_{313}$	$c_{314}$	$c_{315}$	$c_{316}$	$c_{317}$	$c_{318}$	$c_{319}$	$c_{320}$	$c_{321}$	$c_{322}$	$c_{323}$	$c_{324}$	$c_{325}$	$c_{326}$	$c_{327}$	$c_{328}$	$c_{329}$	$c_{330}$	$c_{331}$	$c_{332}$	$c_{333}$	$c_{334}$	$c_{335}$	$c_{336}$	$c_{337}$	$c_{338}$	$c_{339}$	$c_{340}$	$c_{341}$	$c_{342}$	$c_{343}$	$c_{344}$	$c_{345}$	$c_{346}$	$c_{347}$	$c_{348}$	$c_{349}$	$c_{350}$	$c_{351}$	$c_{352}$	$c_{353}$	$c_{354}$	$c_{355}$	$c_{356}$	$c_{357}$	$c_{358}$	$c_{359}$	$c_{360}$	$c_{361}$	$c_{362}$	$c_{363}$	$c_{364}$	$c_{365}$	$c_{366}$	$c_{367}$	$c_{368}$	$c_{369}$	$c_{370}$	$c_{371}$	$c_{372}$	$c_{373}$	$c_{374}$	$c_{375}$	$c_{376}$	$c_{377}$	$c_{378}$	$c_{379}$	$c_{380}$	$c_{381}$	$c_{382}$	$c_{383}$	$c_{384}$	$c_{385}$	$c_{386}$	$c_{387}$	$c_{388}$	$c_{389}$	$c_{390}$	$c_{391}$	$c_{392}$	$c_{393}$	$c_{394}$	$c_{395}$	$c_{396}$	$c_{397}$	$c_{398}$	$c_{399}$	$c_{400}$	$c_{401}$	$c_{402}$	$c_{403}$	$c_{404}$	$c_{405}$	$c_{406}$	$c_{407}$	$c_{408}$	$c_{409}$	$c_{410}$	$c_{411}$	$c_{412}$	$c_{413}$	$c_{414}$	$c_{415}$	$c_{416}$	$c_{417}$	$c_{418}$	$c_{419}$	$c_{420}$	$c_{421}$	$c_{422}$	$c_{423}$	$c_{424}$	$c_{425}$	$c_{426}$	$c_{427}$	$c_{428}$	$c_{429}$	$c_{430}$	$c_{431}$	$c_{432}$	$c_{433}$	$c_{434}$	$c_{435}$	$c_{436}$	$c_{437}$	$c_{438}$	$c_{439}$	$c_{440}$	$c_{441}$	$c_{442}$	$c_{443}$	$c_{444}$	$c_{445}$	$c_{446}$	$c_{447}$	$c_{448}$	$c_{449}$	$c_{450}$	$c_{451}$	$c_{452}$	$c_{453}$	$c_{454}$	$c_{455}$	$c_{456}$	$c_{457}$	$c_{458}$	$c_{459}$	$c_{460}$	$c_{461}$	$c_{462}$	$c_{463}$	$c_{464}$	$c_{465}$	$c_{466}$	$c_{467}$	$c_{468}$	$c_{469}$	$c_{470}$	$c_{471}$	$c_{472}$	$c_{473}$	$c_{474}$	$c_{475}$	$c_{476}$	$c_{477}$	$c_{478}$	$c_{479}$	$c_{480}$	$c_{481}$	$c_{482}$	$c_{483}$	$c_{484}$	$c_{485}$	$c_{486}$	$c_{487}$	$c_{488}$	$c_{489}$	$c_{490}$	$c_{491}$	$c_{492}$	$c_{493}$	$c_{494}$	$c_{495}$	$c_{496}$	$c_{497}$	$c_{498}$	$c_{499}$	$c_{500}$	$c_{501}$	$c_{502}$	$c_{503}$	$c_{504}$	$c_{505}$	$c_{506}$	$c_{507}$	$c_{508}$	$c_{509}$	$c_{510}$	$c_{511}$	$c_{512}$	$c_{513}$	$c_{514}$	$c_{515}$	$c_{516}$	$c_{517}$	$c_{518}$	$c_{519}$	$c_{520}$	$c_{521}$	$c_{522}$	$c_{523}$	$c_{524}$	$c_{525}$	$c_{526}$	$c_{527}$	$c_{528}$	$c_{529}$	$c_{530}$	$c_{531}$	$c_{532}$	$c_{533}$	$c_{534}$	$c_{535}$	$c_{536}$	$c_{537}$	$c_{538}$	$c_{539}$	$c_{540}$	$c_{541}$	$c_{542}$	$c_{543}$	$c_{544}$	$c_{545}$	$c_{546}$	$c_{547}$	$c_{548}$	$c_{549}$	$c_{550}$	$c_{551}$	$c_{552}$	$c_{553}$	$c_{554}$	$c_{555}$	$c_{556}$	$c_{557}$	$c_{558}$	$c_{559}$	$c_{560}$	$c_{561}$	$c_{562}$	$c_{563}$	$c_{564}$	$c_{565}$	$c_{566}$	$c_{567}$	$c_{568}$	$c_{569}$	$c_{570}$	$c_{571}$	$c_{572}$	$c_{573}$	$c_{574}$	$c_{575}$	$c_{576}$	$c_{577}$	$c_{578}$	$c_{579}$	$c_{580}$	$c_{581}$	$c_{582}$	$c_{583}$	$c_{584}$	$c_{585}$	$c_{586}$	$c_{587}$	$c_{588}$	$c_{589}$	$c_{590}$	$c_{591}$	$c_{592}$	$c_{593}$	$c_{594}$	$c_{595}$	$c_{596}$	$c_{597}$	$c_{598}$	$c_{599}$	$c_{600}$	$c_{601}$	$c_{602}$	$c_{603}$	$c_{604}$	$c_{605}$	$c_{606}$	$c_{607}$	$c_{608}$	$c_{609}$	$c_{610}$	$c_{611}$	$c_{612}$	$c_{613}$	$c_{614}$	$c_{615}$	$c_{616}$	$c_{617}$	$c_{618}$	$c_{619}$	$c_{620}$	$c_{621}$	$c_{622}$	$c_{623}$	$c_{624}$	$c_{625}$	$c_{626}$	$c_{627}$	$c_{628}$	$c_{629}$	$c_{630}$	$c_{631}$	$c_{632}$	$c_{633}$	$c_{634}$	$c_{635}$	$c_{636}$	$c_{637}$	$c_{638}$	$c_{639}$	$c_{640}$	$c_{641}$	$c_{642}$	$c_{643}$	$c_{644}$	$c_{645}$	$c_{646}$	$c_{647}$	$c_{648}$	$c_{649}$	$c_{650}$	$c_{651}$	$c_{652}$	$c_{653}$	$c_{654}$	$c_{655}$	$c_{656}$	$c_{657}$	$c_{658}$	$c_{659}$	$c_{660}$	$c_{661}$	$c_{662}$	$c_{663}$	$c_{664}$	$c_{665}$	$c_{666}$	$c_{667}$	$c_{668}$	$c_{669}$	$c_{670}$	$c_{671}$	$c_{672}$	$c_{673}$	$c_{674}$	$c_{675}$	$c_{676}$	$c_{677}$	$c_{678}$	$c_{679}$	$c_{680}$	$c_{681}$	$c_{682}$	$c_{683}$	$c_{684}$	$c_{685}$	$c_{686}$	$c_{687}$	$c_{688}$	$c_{689}$	$c_{690}$	$c_{691}$	$c_{692}$	$c_{693}$	$c_{694}$	$c_{695}$	$c_{696}$	$c_{697}$	$c_{698}$	$c_{699}$	$c_{700}$	$c_{701}$	$c_{702}$	$c_{703}$	$c_{704}$	$c_{705}$	$c_{706}$	$c_{707}$	$c_{708}$	$c_{709}$	$c_{710}$	$c_{711}$	$c_{712}$	$c_{713}$	$c_{714}$	$c_{715}$	$c_{716}$	$c_{717}$	$c_{718}$	$c_{719}$	$c_{720}$	$c_{721}$	$c_{722}$	$c_{723}$	$c_{724}$	$c_{725}$	$c_{726}$	$c_{727}$	$c_{728}$	$c_{729}$	$c_{730}$	$c_{731}$	$c_{732}$	$c_{733}$	$c_{734}$	$c_{735}$	$c_{736}$	$c_{737}$	$c_{738}$	$c_{739}$	$c_{740}$	$c_{741}$	$c_{742}$	$c_{743}$	$c_{744}$	$c_{745}$	$c_{746}$	$c_{747}$	$c_{748}$	$c_{749}$	$c_{750}$	$c_{751}$	$c_{752}$	$c_{753}$	$c_{754}$	$c_{755}$	$c_{756}$	$c_{757}$	$c_{758}$	$c_{759}$	$c_{760}$	$c_{761}$	$c_{762}$	$c_{763}$	$c_{764}$	$c_{765}$	$c_{766}$	$c_{767}$	$c_{768}$	$c_{769}$	$c_{770}$	$c_{771}$	$c_{772}$	$c_{773}$	$c_{774}$	$c_{775}$	$c_{776}$	$c_{777}$	$c_{778}$	$c_{779}$	$c_{780}$	$c_{781}$	$c_{782}$	$c_{783}$	$c_{784}$	$c_{785}$	$c_{786}$	$c_{787}$	$c_{788}$	$c_{789}$	$c_{790}$	$c_{791}$	$c_{792}$	$c_{793}$	$c_{794}$	$c_{795}$	$c_{796}$	$c_{797}$	$c_{798}$	$c_{799}$	$c_{800}$	$c_{801}$	$c_{802}$	$c_{803}$	$c_{804}$	$c_{805}$	$c_{806}$	$c_{807}$	$c_{808}$	$c_{809}$	$c_{810}$	$c_{811}$	$c_{812}$	$c_{813}$	$c_{814}$	$c_{815}$	$c_{816}$	$c_{817}$	$c_{818}$	$c_{819}$	$c_{820}$	$c_{821}$	$c_{822}$	$c_{823}$	$c_{824}$	$c_{825}$	$c_{826}$	$c_{827}$	$c_{828}$	$c_{829}$	$c_{830}$	$c_{831}$	$c_{832}$	$c_{833}$	$c_{834}$	$c_{835}$	$c_{836}$	$c_{837}$	$c_{838}$	$c_{839}$	$c_{840}$	$c_{841}$	$c_{842}$	$c_{843}$	$c_{844}$	$c_{845}$	$c_{846}$	$c_{847}$	$c_{848}$	$c_{849}$	$c_{850}$	$c_{851}$	$c_{852}$	$c_{853}$	$c_{854}$	$c_{855}$	$c_{856}$	$c_{857}$	$c_{858}$	$c_{859}$	$c_{860}$	$c_{861}$	$c_{862}$	$c_{863}$	$c_{864}$	$c_{865}$	$c_{866}$	$c_{867}$	$c_{868}$	$c_{869}$	$c_{870}$	$c_{871}$	$c_{872}$	$c_{873}$	$c_{874}$	$c_{875}$	$c_{876}$	$c_{877}$	$c_{878}$	$c_{879}$	$c_{880}$	$c_{881}$	$c_{882}$	$c_{883}$	$c_{884}$	$c_{885}$	$c_{886}$	$c_{887}$	$c_{888}$	$c_{889}$	$c_{890}$	$c_{891}$	$c_{892}$	$c_{893}$	$c_{894}$	$c_{895}$	$c_{896}$	$c_{897}$	$c_{898}$	$c_{899}$	$c_{900}$	$c_{901}$	$c_{902}$	$c_{903}$	$c_{904}$	$c_{905}$	$c_{906}$	$c_{907}$	$c_{908}$	$c_{909}$	$c_{910}$	$c_{911}$	$c_{912}$	$c_{913}$	$c_{914}$	$c_{915}$	$c_{916}$	$c_{917}$	$c_{918}$	$c_{919}$	$c_{920}$	$c_{921}$	$c_{922}$	$c_{923}$	$c_{924}$	$c_{925}$	$c_{926}$	$c_{927}$	$c_{928}$	$c_{929}$	$c_{930}$	$c_{931}$	$c_{932}$	$c_{933}$	$c_{934}$	$c_{935}$	$c_{936}$	$c_{937}$	$c_{938}$	$c_{939}$	$c_{940}$	$c_{941}$	$c_{942}$	$c_{943}$	$c_{944}$	$c_{945}$	$c_{94$
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ALCOHOLS ( $C_nH_{2n+2}O_m$ ,  $n=1,2,3,4,5\ldots\infty$ )

The alkyl alcohols,  $C_nH_{2n+2}O_m$ , comprise an  $OH$  functional group and two types of  $C-O$  functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The  $OH$  functional group was solved in the Hydroxyl Radical ( $OH$ ) section. Each  $C-O$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $O$  AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO \text{ to } O) = \frac{E(O)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.85395 \quad (15.114)$$

$E_r(atom - atom, msp^3.AO)$  of the  $C-O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-1.65376 \text{ eV}$  for the  $CH_3-OH$   $C-O$  group. It is based on the energy match between the  $OH$  group and the  $C2sp^3$  HO of a methyl group and is given by the linear combination of  $-0.92918 \text{ eV}$  (Eq. (14.513)) and  $-0.72457 \text{ eV}$  (Eq. (14.151)), respectively. For the alkyl  $C-O$  group,  $E_r(atom - atom, msp^3.AO)$  is  $-1.85836 \text{ eV}$ . It is based on the energy match between the  $O$  AO and the  $C2sp^3$  HO of a methylene group where both energy contributions are given by Eq. (14.513).



The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.57. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 5 15.61 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.79-15.108) are given in Table 15.62.



Table 15.58. The geometrical bond parameters of alkyl alcohols and experimental values [1].

Functional Group	Group Symbol
OH group	OH
CH <sub>3</sub> OH C-O	C-O (i)
Alkyl C-O	C-O (ii)
CH <sub>3</sub> group	C'-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C'-C' (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C' (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C' (e)
CC (t to iso-C)	C-C' (f)

Table 15.58. The geometrical bond parameters of alkyl alcohols and experimental values [1].

Parameter	OH Group	C-O (i) Group	C-O (ii) Group	C'-H (CH <sub>3</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\alpha$ ( $^\circ$ )	1.26430	1.79473	1.78255	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$\alpha'$ ( $^\circ$ )	0.91808	1.33968	1.33512	1.04856	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ( $\text{\AA}$ )	0.971651	1.41785	1.41303	1.10974	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ( $\text{\AA}$ )	0.971 (ethanol) 0.9451 (methanol)	1.4246 (methanol)	1.431 (ethanol)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c$ ( $^\circ$ )	0.86925	1.19429	1.18107	1.27295	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.72615	0.74645	0.74900	0.63580	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.59. The MO to HO intercept geometrical bond parameters of alkyl alcohols.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C_{2sp^3}$ (eV)	$r_{\text{mwp}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{Coulomb}}$ (eV) Final	$E(C_{2sp^3})$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$H_2CO-H$	O	-0.82688	0	0	0		1.00000	0.86923	-15.65263		115.49	64.51	64.51	0.54405	0.37403
$-H_2C-O-H$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		115.09	64.91	64.12	0.55182	0.36625
$H_2C-OH$	C	-0.82688	0	0	0	-152.44257	0.91771	0.86923	-15.65263	-15.46177	96.59	83.41	46.30	1.23986	0.09981
$H_2C-OH$	O	-0.82688	0	0	0		1.00000	0.86923	-15.65263		96.59	83.41	46.30	1.23986	0.09981
$(C-O \text{ (i)})$															
$-H_2C-OH$	C	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	93.09	86.91	43.59	1.29114	0.04398
$-H_2C-OH$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		97.20	82.80	46.50	1.22692	0.10820
$(C-O \text{ (ii)})$															
$C-H (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_2C-C_2H_5$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$(C-C \text{ (a)})$															
$H_2C-C_2H_5$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	121.59	26.06	1.90890	0.45117
$(C-C \text{ (b)})$															
$R-H_2C-C_2H_5$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(C-C \text{ (c)})$															
$R-H_2C-C_2H_5$	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(C-C \text{ (d)})$															
$R-H_2C-C_2H_5$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(C-C \text{ (e)})$															
$R-H_2C-C_2H_5$	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$(C-C \text{ (f)})$															
$R-H_2C-C_2H_5$	C	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$(C-C \text{ (g)})$															
$R-H_2C-C_2H_5$	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.60. The energy parameters (eV) of functional groups of alkyl alcohols.

Parameters	OH Group	C-O (i) Group	C-O (ii) Group	C-H <sub>3</sub> Group	C-H <sub>3</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$n_1$	1	1	1	2	3	1	1	1	1	1	1	1
$n_2$	0	0	0	1	2	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1	1
$C_3$	0.75	1	1	1	1	1	1	1	1	1	1	1
$C_4$	1	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	1	0	0	1	0	1	0	0	0	1	1	0
$C_6$	1	2	2	1	1	1	2	2	2	2	2	2
$C_7$	1	0	0	3	3	1	0	0	0	0	0	0
$C_{100}$	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C'_{20}$	1	1	1	1	1	1	1	1	1	1	1	1
$V'_p$ (eV)	-40.92709	-33.47304	-33.78820	-70.41425	-107.32728	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p$ (eV)	14.81988	10.15605	10.19068	25.78002	38.92728	12.87680	9.33552	9.33552	9.37273	9.33552	9.37273	9.37273
$T$ (eV)	16.18567	9.32537	9.47749	21.06675	32.53914	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V''_m$ (eV)	-8.09284	-4.66268	-4.73874	-10.53337	-16.26957	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E'_{(w\text{ in})}$ (eV)	-13.6181	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.55946	-15.56407	-15.55946	-15.55946
$\Delta E'_{(w\text{ in})}$ (eV)	0	-1.65376	-1.85836	0	0	0	0	0	0	0	0	0
$E'_{(w\text{ in})}$ (eV)	-13.6181	-12.98113	-12.77653	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.55946	-15.56407	-15.55946	-15.55946
$E'_{(w\text{ in})}$ (eV)	-31.63247	-31.63544	-31.63529	-49.66493	-67.69451	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E'_{(atom-atom,exp,DO)}$ (eV)	0	-1.65376	-1.85836	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E'_{(w\text{ in})}$ (eV)	-31.63537	-33.28912	-33.49373	-49.66493	-67.69450	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^6$ rad/s)	44.1776	22.3978	12.2831	24.2751	24.9286	24.1759	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E'_k$ (eV)	29.07844	14.74264	8.08494	16.40846	16.40846	15.97831	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E'_{k1}$ (eV)	-0.33749	-0.25287	-0.18841	-0.25352	-0.25352	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E'_{k2k}$ (eV)	0.46311	0.12808	0.13328	0.35532	0.35532	0.35532	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
$E'_{k2k}$ (eV)	[17-18]	[19]	[20]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[21]	[4]	[5]	[21]	[2]	[2]
$E'_{k2k}$ (eV)	-0.10594	-0.18883	-0.12177	-0.14502	-0.22757	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E'_{k2k}$ (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E'_{k2k}$ (eV)	-31.74130	-33.47795	-33.61550	-49.80996	-67.92207	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E'_{k2k}$ (eV)	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E'_{k2k}$ (eV)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E'_{k2k}$ (eV)	4.41035	4.20817	4.34572	7.83016	12.49186	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734



Table 15.61. The total bond energies of alkyl alcohols calculated using the functional group composition and the energies of Table 15.60 compared to the experimental values [3].

Formula	Name	OH Group	C-O (i) Group	C-O (ii) Group	CH <sub>3</sub>	CH <sub>2</sub>	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>4</sub> O	Methanol	1	0	1	1	0	0	0	0	0	0	0	0	21.11038	21.131	0.00097
C <sub>2</sub> H <sub>6</sub> O	Ethanol	1	0	1	1	1	0	0	0	0	0	0	0	33.40563	33.428	0.00066
C <sub>3</sub> H <sub>8</sub> O	1-Propanol	1	0	1	1	2	0	2	0	0	0	0	0	45.56333	45.584	0.00046
C <sub>3</sub> H <sub>8</sub> O	2-Propanol	1	0	1	2	0	1	2	0	0	0	0	0	45.72088	45.766	0.00098
C <sub>4</sub> H <sub>10</sub> O	1-Butanol	1	0	1	1	3	0	3	0	0	0	0	0	57.72103	57.736	0.00026
C <sub>4</sub> H <sub>10</sub> O	2-Butanol	1	0	1	2	1	1	3	0	0	0	0	0	57.87858	57.922	0.00074
C <sub>4</sub> H <sub>10</sub> O	2-Methyl-1-propananol	1	0	1	2	1	1	0	3	0	0	0	0	57.79359	57.828	0.00060
C <sub>4</sub> H <sub>10</sub> O	2-Methyl-2-propananol	1	0	1	3	0	0	0	3	0	0	0	0	58.15359	58.126	-0.00048
C <sub>5</sub> H <sub>12</sub> O	1-Pentanol	1	0	1	1	4	0	4	0	0	0	0	0	69.87873	69.887	0.00011
C <sub>5</sub> H <sub>12</sub> O	2-Pentanol	1	0	1	2	2	1	4	0	0	0	0	0	70.03628	70.057	0.00029
C <sub>5</sub> H <sub>12</sub> O	3-Pentanol	1	0	1	2	2	1	4	0	0	0	0	0	70.03628	70.097	0.00087
C <sub>5</sub> H <sub>12</sub> O	2-Methyl-1-butanol	1	0	1	2	2	1	2	3	0	0	0	0	69.95129	69.957	0.00008
C <sub>5</sub> H <sub>12</sub> O	3-Methyl-1-butanol	1	0	1	2	2	1	1	3	0	0	0	0	69.95129	69.950	-0.00002
C <sub>5</sub> H <sub>12</sub> O	2-Methyl-2-butanol	1	0	1	3	1	0	1	3	0	0	0	0	70.31129	70.246	-0.00092
C <sub>5</sub> H <sub>12</sub> O	3-Methyl-2-butanol	1	0	1	3	0	2	0	3	0	1	0	0	69.96081	70.083	0.00174
C <sub>6</sub> H <sub>14</sub> O	1-Hexanol	1	0	1	1	5	0	5	0	0	0	0	0	82.03643	82.054	0.00021
C <sub>6</sub> H <sub>14</sub> O	2-Hexanol	1	0	1	2	3	1	5	0	0	0	0	0	82.19398	82.236	0.00052
C <sub>6</sub> H <sub>14</sub> O	3-Hexanol	1	0	1	2	3	1	5	0	0	0	0	0	82.19398	82.236	0.00052
C <sub>7</sub> H <sub>16</sub> O	1-Heptanol	1	0	1	1	6	0	6	0	0	0	0	0	94.19413	94.214	0.00021
C <sub>7</sub> H <sub>16</sub> O	2-Heptanol	1	0	1	1	7	0	7	0	0	0	0	0	106.35183	106.358	0.00006
C <sub>7</sub> H <sub>16</sub> O	3-Heptanol	1	0	1	2	13	1	4	3	0	0	0	0	106.42439	106.459	0.00032
C <sub>8</sub> H <sub>18</sub> O	1-Octanol	1	0	1	1	8	0	8	0	0	0	0	0	118.50953	118.521	0.00010
C <sub>8</sub> H <sub>18</sub> O	2-Octanol	1	0	1	1	9	0	9	0	0	0	0	0	130.66723	130.676	0.00007
C <sub>9</sub> H <sub>20</sub> O	1-Nonanol	1	0	1	1	11	0	11	0	0	0	0	0	154.98263	154.984	0.00001
C <sub>10</sub> H <sub>22</sub> O	1-Decanol	1	0	1	1	11	0	11	0	0	0	0	0	203.61343	203.603	-0.00005
C <sub>12</sub> H <sub>26</sub> O	1-Dodecanol	1	0	1	1	15	0	15	0	0	0	0	0			
C <sub>16</sub> H <sub>34</sub> O	1-Hexadecanol	1	0	1	1	15	0	15	0	0	0	0	0			







ETHERS ( $C_nH_{2n+2}O_m$ ,  $n=2,3,4,5\ldots\infty$ )

The alkyl ethers,  $C_nH_{2n+2}O_m$ , comprise two types of  $C-O$  functional groups, one for methyl or t-butyl groups corresponding to the  $C$  and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups ( $CH_3$ ) at each  
 5 end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the  
 10 isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each  $C-O$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO  
 15 and the  $O$  AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of  $E(C,2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  
 20  $C-O$ -bond MO given by Eq. (15.113) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ .  $E_r(\text{atom-atom}, msp^3.AO)$  of the  $C-O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-1.44915 \text{ eV}$  for the  $CH_3-O-$  and  $(CH_3)_3C-O-$   $C-O$  groups. It is based on the energy match between the  $O$  AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), and the  $C2sp^3$   
 25 HO of a methyl group as given by Eq. (14.151). For the alkyl  $C-O$  group,  $E_r(\text{atom-atom}, msp^3.AO)$  is  $-1.65376 \text{ eV}$ . It is based on the energy match between the  $O$  AO and the  $C2sp^3$  HO of a methylene group and is given by the linear combination of  $-0.72457 \text{ eV}$  (Eq. (14.151)) and  $-0.92918 \text{ eV}$  (Eq. (14.513)), respectively.



The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67  
5 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.79-15.108) are given in Table 15.68.



Table 15.63. The symbols of functional groups of alkyl ethers.

Functional Group	Group Symbol
C-O ( $\text{CH}_3$ -O- and $(\text{CH}_3)_3\text{C-O-}$ )	C-O (i)
C-O (alkyl)	C-O (ii)
$\text{CH}_3$ group	C-H ( $\text{CH}_3$ )
$\text{CH}_2$ group	C-H ( $\text{CH}_2$ )
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.64. The geometrical bond parameters of alkyl ethers and experimental values [1].

Parameter	C-O (i) Group	C-O (ii) Group	C-H ( $\text{CH}_3$ ) Group	C-H ( $\text{CH}_2$ ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a$ ( $a_0$ )	1.80717	1.79473	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ ( $a_0$ )	1.34431	1.33968	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ( $\text{\AA}$ )	1.42276	1.41785	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ( $\text{\AA}$ )	1.416 (dimethyl ether)	1.418 (ethyl methyl ether (avg.))	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c$ ( $a_0$ )	1.20776	1.19429	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.74388	0.74645	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888







Table 15.66. The energy parameters (eV) of functional groups of alkyl ethers.

Parameters	C-O (i) Group	C-O (ii) Group	H <sub>2</sub> Group	H <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0
$\zeta_1$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_2$	1	1	1	1	1	1	1	1	1	1	1
$\zeta_3$	1	1	1	1	1	1	1	1	1	1	1
$\zeta_4$	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\zeta_5$	0	0	0	1	1	0	0	0	1	1	0
$\zeta_6$	2	2	1	1	1	2	2	2	2	2	2
$\zeta_7$	0	0	3	2	1	0	0	0	0	0	0
$\zeta_8$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_9$	1	1	1	1	1	1	1	1	1	1	1
$\zeta_{10}$	-33.15757	-33.47304	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_c$ (eV)	10.12105	10.15605	38.92728	25.78002	12.87680	9.33552	9.33552	9.37273	9.33552	9.37273	9.37273
$V_r$ (eV)	9.17389	9.32537	32.33914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_n$ (eV)	-4.58695	-4.66268	-16.26957	-10.53537	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{1,0}$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{1,0}$ (eV)	-1.44915	-1.65376	0	0	0	0	0	0	0	0	0
$E_{1,0}^{(a)}$ (eV)	-13.18574	-12.98113	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{1,0}^{(b)}$ (eV)	-31.63553	-31.63544	-67.69451	-49.66493	-31.63553	-31.63553	-31.63553	-31.63553	-31.63553	-31.63553	-31.63553
$E_{1,0}^{(c)}$ (eV)	-1.44915	-1.65376	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{1,0}^{(d)}$ (eV)	-33.08452	-33.28912	-67.69450	-49.66493	-31.63553	-33.49573	-33.49573	-33.08452	-33.49573	-33.08452	-33.08452
$\omega$ (10 <sup>15</sup> rad/s)	12.0329	12.1583	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{1,0}^{(e)}$ (eV)	7.92028	8.00277	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{1,0}^{(f)}$ (eV)	-0.18420	-0.18631	-0.25552	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{1,0}^{(g)}$ (eV)	0.13663	0.16118	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{1,0}^{(h)}$ (eV)	-0.11589	-0.10572	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{1,0}^{(i)}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{1,0}^{(j)}$ (eV)	-33.20040	-33.39484	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24576	-33.59732	-33.18712	-33.18712
$E_{1,0}^{(k)}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{1,0}^{(l)}$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{1,0}^{(m)}$ (eV)	3.93062	4.12506	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734



Table 15.67. The total bond energies of alkyl ethers calculated using the functional group composition and the energies of Table 15.66 compared to the experimental values [3].

Formula	Name	Group	$C-O$ (i)	Group	$C-H$	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6O$	Dimethyl ether	2	0	2	0	0	0	0	0	0	0	32.8496	32.902	0.00174
$C_3H_8O$	Ethyl methyl ether	1	1	2	0	1	0	0	0	0	0	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	0	2	2	0	2	0	0	0	0	0	57.54924	57.500	-0.00086
$C_5H_{12}O$	Methyl propyl ether	1	1	2	0	2	0	0	0	0	0	57.35480	57.355	0.00000
$C_6H_{14}O$	Isopropyl methyl ether	0	2	3	0	0	2	0	0	0	0	57.45569	57.499	0.00075
$C_6H_{14}O$	Diisopropyl ether	0	2	2	0	4	0	0	0	0	0	81.86464	81.817	-0.00059
$C_7H_{16}O$	Disopropyl ether	0	2	4	0	0	4	0	0	0	0	82.06642	82.088	0.00026
$C_8H_{18}O$	t-Butyl ethyl ether	1	1	4	0	1	0	3	0	0	0	82.10276	82.033	-0.00085
$C_8H_{18}O$	t-Butyl isopropyl ether	1	1	5	0	1	0	3	0	0	0	94.36135	94.438	0.00081
$C_8H_{18}O$	Dibutyl ether	0	2	2	0	6	0	0	0	0	0	106.18004	106.122	-0.00055
$C_9H_{20}O$	Di-sec-butyl ether	0	2	4	0	2	4	0	0	0	0	106.38182	106.410	0.00027
$C_9H_{20}O$	Di-tert-butyl ether	2	0	6	0	0	0	6	0	0	0	106.55628	106.425	-0.00218
$C_{10}H_{22}O$	t-Butyl isobutyl ether	1	1	5	0	1	3	0	0	0	0	106.49072	106.497	0.00005

Table 15.68. The bond angle parameters of alkyl ethers and experimental values [1]. In the calculation of  $\theta_p$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, A(\theta))$ .

Atom of Angle	$2c'$ Bond 1 ( $a_1$ )	$2c'$ Bond 2 ( $a_2$ )	$2c'$ Terminal Atom ( $a_3$ )	$I_{\text{calc}}$ Atom 1	$I_{\text{calc}}$ Atom 2	Hybridization Designation (Table 15.3.A)	$C_2$ Atom 1	$C_2$ Atom 2	$C_1$	$C_2$	$C_1$	$C_2$	$E_T$ (eV)	$\theta_p$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	Cal. $\theta$ (°)	Exp. $\theta$ (°)
$\angle C'_1 O C'_2$ ( $C'_1 - O - C'_2$ ) (i)	2.68602	2.68602	4.4721	-17.40869	-17.40869	38	0.78155	0.78155	1	1	1	0.78155	-1.85836				112.54	112 (dimethyl ether)
$\angle C'_1 O C'_2$ ( $C'_1 - O - C'_2$ ) (ii)	2.68602	2.67935	4.4385	-17.31099	-17.31099	41	0.77699	0.77699	1	1	1	0.77699	-1.85836				111.55	111.9 (ethyl methyl ether)
$\angle C'_1 C'_2 C'_3$ ( $C'_1 - C'_2 - C'_3$ ) (i)	2.91547	2.67935	4.5607	-16.68412	-15.61806	0	0.81549	0.83595 (Eq. 15.11.4)	1	1	1	0.83472	-1.65376				109.13	109.4 (ethyl methyl ether)
$\angle C'_1 C'_2 C'_3$ ( $C'_1 - C'_2 - C'_3$ ) (ii)	2.11106	2.11106	3.4252	-15.75493	-15.75493	7	0.86559	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C'_1 C'_2 C'_3$														69.51			110.49	115.8 (propane) 110.8 (isobutane) 111.0 (isobutane)
$\angle C'_1 C'_2 H$														69.51			110.49	111.4 (isobutane)
Methyl $\angle C'_1 C'_2 H$	2.09711	2.09711	3.4252	-15.75493	-15.75493	7	0.86559	1	1	1	0.75	1.15796	0				109.50	
$\angle C'_1 C'_2 C'_3$														70.56			109.44	
$\angle C'_1 C'_2 C'_3$														70.56			109.44	
$\angle C'_1 C'_2 C'_3$ iso $C'_3$	2.91547	2.91547	4.7958	-16.68412	-16.68412	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C'_1 C'_2 H$	2.91547	2.11323	4.1633	-15.50033	-14.82575	5	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C'_1 C'_2 H$	2.91547	2.09711	4.1633	-15.50033	-14.82575	5	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C'_1 C'_2 C'_3$ iso $C'_3$	2.90327	2.90327	4.7958	-15.50033	-14.82575	5	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C'_1 C'_2 C'_3$														72.50			107.50	



PRIMARY AMINES ( $C_n H_{2n+2+m} N_m$ ,  $n=1,2,3,4,5\ldots\infty$ )

The primary amines,  $C_n H_{2n+2+m} N_m$ , comprise an  $NH_2$  functional group and a  $C-N$  functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and  
 5 methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  
 10  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino ( $NH_2$ ) functional group was solved using the procedure given in the Dihydrogen Nitride ( $NH_2$ ) section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.52) are  $n_1 = 2$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  
 15  $C_{10} = 1.5$ , and  $c_1 = 0.75$ . In primary amines, the  $C2sp^3$  HO of the  $C-NH_2$ -bond MO has an energy of  $E(C, 2sp^3) = -15.35946 \text{ eV}$  (Eq. (15.18) with  $s=1$  and Eqs. (15.19-15.20)) and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $N-H$   $H_2$ -type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  of Eq. (15.52) for the  $N-H$ -bond MO given by Eq. (15.68) is

$$20 \quad c_2(H \text{ to } 1^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627 \quad (15.115)$$

The  $C-N$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a  
 25 corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the



$C-N$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-N$ -bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO \text{ to } N) = \frac{E(N)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.91140 \quad (15.116)$$

$E_T(atom - atom, msp^3.AO)$  of the  $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.44915 \text{ eV}$ . It is based on the energy match between the  $N$  of the  $NH_2$  group and the  $C2sp^3$  HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)), where the  $N-H$  bonds are also energy matched to the  $C-N$  bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.79-15.108) are given in Table 15.74.

Table 15.69. The symbols of functional groups of primary amines.

Functional Group	Group Symbol
$NH_2$ group	$NH_2$
C-N	$C-N$
$CH_3$ group	$C-H (CH_3)$
$CH_2$ group	$C-H (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)



Table 15.70. The geometrical bond parameters of primary amines and experimental values [1].

Parameter	$NH_2$ Group	$C-N$ Group	$C-H$ Group	$C-H$ Group	$C-C$ Group	$C-C$ Group	$C-C$ Group	$C-C$ Group	$C-C$ Group	$C-C$ Group
$a$ ( $a_0$ )	1.28083	1.92682	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.10725	2.10725
$c'$ ( $a_0$ )	0.95506	1.38810	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45164	1.45164
Bond Length $2c'$ ( $\text{\AA}$ )	1.0108	1.0974	1.11713	1.11827	1.11827	1.54280	1.54280	1.53635	1.53635	1.53635
Exp. Bond Length ( $\text{\AA}$ )	1.010 (methylamine)	1.471 (methylamine)	1.107 ( $C-H$ propane) 1.117 ( $C-H$ butane)	1.122 (isobutane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b_{1c}$ ( $a_0$ )	0.85345	1.33634	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.52750	1.52750
$e$	0.74566	0.72041	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68888	0.68888

Table 15.71. The MO to HO intercept geometrical bond parameters of primary amines.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C2_{sp^3}$ (eV)	$r_{ind}$ ( $a_0$ )	$r_{ind}$ ( $a_0$ )	$E_{C_{2sp^3}}$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$H_2C(NH) - H$	N	-0.72457	0	0	0	-15.55033	0.93084	0.87495	-15.55033	118.00	62.00	64.85	0.54432	0.41075
$-H_2C(NH) - H$	N	-0.72457	0	0	0	-15.55033	0.93084	0.87495	-15.55033	118.00	62.00	64.85	0.54432	0.41075
$H_2C - NH_2$	C	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-153.5946	85.28	94.72	40.73	1.46010	0.07200
$H_2C - NH_2$	N	-0.72457	0	0	0	-15.55033	0.93084	0.87495	-15.55033	85.28	94.72	40.73	1.46010	0.07200
$-H_2C - NH_2$	C	-0.72457	-0.92918	0	0	-153.25945	0.91771	0.82562	-16.47951	80.20	99.80	37.50	1.52858	0.14048
$-H_2C - NH_2$	N	-0.72457	0	0	0	-15.55033	0.93084	0.87495	-15.55033	85.28	94.72	40.73	1.46010	0.07200
$C - H$ ( $CH_3$ )	C	-0.92918	0	0	0	-152.34487	0.91771	0.86359	-15.75493	77.49	102.51	41.48	1.23564	0.18708
$C - H$ ( $CH_3$ )	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	68.47	111.53	35.84	1.3486	0.29933
$C - H$ ( $CH$ )	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	61.10	118.90	31.37	1.42988	0.37326
$H_2C, C, H_2, CH_2 -$ ( $C - C$ )	C	-0.92918	0	0	0	-152.34487	0.91771	0.86359	-15.75493	63.82	116.18	30.08	1.83879	0.38106
$H_2C, C, H_2, CH_2 -$ ( $C - C$ )	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	56.41	123.59	26.06	1.90890	0.45117
$R - H_2C, C, (H_2C - R)HCH_2 -$ ( $C - C$ )	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C, C, (R' - H_2C)C, (R'' - H_2C)CH_2 -$ ( $C - C$ )	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.73889	-17.92866	48.21	131.79	21.74	1.95734	0.50570
$R - H_2C, C, (H_2C - R)HCH_2 -$ ( $C - C$ )	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C, C, (R' - H_2C)C, (R'' - H_2C)CH_2 -$ ( $C - C$ )	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.51999	0.91771	0.76765	-17.92866	50.04	129.96	22.66	1.94462	0.49298
$R - H_2C, C, (H_2C - R)HCH_2 -$ ( $C - C$ )	C	-0.92918	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	52.78	127.22	24.04	1.92443	0.47279
$R - H_2C, C, (R' - H_2C)C, (R'' - H_2C)CH_2 -$ ( $C - C$ )	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.51999	0.91771	0.76765	-17.92866	50.04	129.96	22.66	1.94462	0.49298



Table 15.72. The energy parameters (eV) of functional groups of primary amines

Parameters	NH <sub>2</sub> Group	C-N Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$n_1$	2	1	3	2	1	1	1	1	1	1	1
$n_2$	0	0	2	1	0	0	0	0	0	0	0
$n_3$	1	0	0	0	0	0	0	0	0	0	0
$C_1$	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	0.93613	1	1	1	1	1	1	1	1	1	1
$C_3$	0.75	1	1	1	1	1	1	1	1	1	1
$C_4$	0.94627	0.91440	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	0	1	1	0	0	0	1	1	0
$C_6$	1	2	1	1	1	2	2	2	2	2	2
$C_7$	2	0	3	2	1	0	0	0	0	0	0
$C_{10}$	1.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{100}$	1	1	1	1	1	1	1	1	1	1	1
$V_c$ (eV)	-77.89807	-32.46339	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_s$ (eV)	28.49191	9.80175	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T$ (eV)	30.40957	8.42409	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_p$ (eV)	-15.20478	-4.21204	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{1,100}^{(1,100)}$ (eV)	-14.53414	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,100}^{(1,100)}$ (eV)	0	-1.44915	0	0	0	0	0	0	0	0	0
$E_{1,100}^{(1,100)}$ (eV)	-14.53414	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{1,100}^{(1,100)}$ (eV)	-14.53414	0	0	0	0	0	0	0	0	0	0
$E_{1,100}^{(1,100)}$ (eV)	-48.73642	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{1,100}^{(1,100)}$ (eV)	0	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{1,100}^{(1,100)}$ (eV)	-48.73660	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ (10 <sup>5</sup> rad/s)	64.2189	18.9231	24.9786	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{1,100}^{(1,100)}$ (eV)	42.27003	12.45552	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{1,100}^{(1,100)}$ (eV)	-0.40690	-0.23100	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{1,100}^{(1,100)}$ (eV)	0.40929	0.12944	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{1,100}^{(1,100)}$ (eV)	122	23	13	13	13	2	2	5	2	2	2
$E_{1,100}^{(1,100)}$ (eV)	-0.20226	-0.16628	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{1,100}^{(1,100)}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{1,100}^{(1,100)}$ (eV)	-49.14112	-33.25079	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24376	-33.59732	-33.18712	-33.18712
$E_{1,100}^{(1,100)}$ (eV)	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{1,100}^{(1,100)}$ (eV)	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{1,100}^{(1,100)}$ (eV)	7.41010	3.98101	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.73. The total bond energies of primary amines calculated using the functional group composition and the energies of Table 15.72 compared to the experimental values [3]

Formula	NH <sub>2</sub> Group	C-N Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	CH Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> N	1	1	1	0	0	0	0	0	0	0	0	23.837	23.837	-0.00110
C <sub>2</sub> H <sub>5</sub> N	1	1	1	1	0	1	0	0	0	0	0	36.0067	36.062	0.00060
C <sub>3</sub> H <sub>7</sub> N	1	1	1	2	0	2	0	0	0	0	0	48.19837	48.243	0.00092
C <sub>4</sub> H <sub>9</sub> N	1	1	1	3	0	3	0	0	0	0	0	60.35007	60.415	0.00098
C <sub>5</sub> H <sub>11</sub> N	1	1	2	0	1	1	2	0	0	0	0	60.45696	60.547	0.00148
C <sub>6</sub> H <sub>13</sub> N	1	1	3	0	0	0	0	3	0	0	0	60.717	60.717	-0.00118
C <sub>7</sub> H <sub>15</sub> N	1	1	2	1	1	0	3	0	0	0	0	60.42863	60.486	0.00094



Table 15.74. The bond angle parameters of primary amines and experimental values [1]. In the calculation of  $\theta_p$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}^3 \cdot \text{AO})$ .

Atoms of Angle	2c' Bond 1 (a <sub>0</sub> )	2c' Bond 2 (a <sub>0</sub> )	2c' Terminal Atoms (a <sub>0</sub> )	E <sub>videhake</sub> or E <sub>2</sub> Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	E <sub>videhake</sub> Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	s <sub>2</sub> Atom 1	s <sub>1</sub> Atom 2	C <sub>1</sub>	C <sub>2</sub>	c <sub>1</sub>	c <sub>2</sub>	E <sub>r</sub> (eV)	θ <sub>r</sub> (°)	θ <sub>1</sub> (°)	θ <sub>2</sub> (°)	Cal. θ (°)	Exp. θ (°)
∠HNH	1.91013	1.91013	3.0984	-14.53414	N	H	H	0.94627 Eq. (15.115)	1	1	1	0.75	1.05679	0				108.40	107.1 (methylamine)
∠HNC <sub>a</sub>	1.91013	2.77620	3.8816	-14.53414	5		N	0.91140 (Eq. (15.116))	0.88583	0.75	1	0.75	0.97194	0				110.48	110.3 (methylamine)
Methylane ∠HC <sub>a</sub> H	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	108.0 (methylamine)
∠C <sub>a</sub> C <sub>b</sub> C <sub>c</sub>																			107 (propane)
∠C <sub>a</sub> C <sub>b</sub> H																			112 (propane)
Methyl ∠HC <sub>a</sub> H	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				110.49	113.8 (butane)
∠C <sub>a</sub> C <sub>b</sub> C <sub>c</sub>																			110.8 (isobutane)
∠C <sub>a</sub> C <sub>b</sub> C <sub>c</sub>	2.91547	2.91547	4.7958	-16.68412	25	C <sub>c</sub>	C <sub>c</sub>	0.81549	0.81549	1	1	1	0.81549	-1.83836				111.0 (isobutane)	111.4 (butane)
∠C <sub>a</sub> C <sub>b</sub> H	2.91547	2.11233	4.1633	-15.55033	5	C <sub>a</sub>	C <sub>b</sub>	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.67	110.8 (isobutane)
∠C <sub>a</sub> C <sub>b</sub> H	2.91547	2.09711	4.1633	-15.55033	5	C <sub>a</sub>	C <sub>b</sub>	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	111.4 (isobutane)
∠C <sub>a</sub> C <sub>b</sub> C <sub>c</sub>	2.90327	2.90327	4.7958	-15.55033	5	C <sub>a</sub>	C <sub>c</sub>	0.87495	0.91771	0.75	1	0.75	1.04887	-1.83836				111.27	111.4 (isobutane)
∠C <sub>a</sub> C <sub>b</sub> C <sub>d</sub>																		107.50	107.50 (isobutane)



SECONDARY AMINES ( $C_n H_{2n+2+m} N_m$ ,  $n = 2, 3, 4, 5 \dots \infty$ )

The secondary amines,  $C_n H_{2n+2+m} N_m$ , comprise an  $NH$  functional group and two types of  $C-N$  functional groups, one for the methyl group corresponding to the  $C$  of  $C-N$  and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may  
 5 comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl  
 10 ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino ( $NH$ ) functional group was solved using the procedure given in the Hydrogen Nitride ( $NH$ ) section. Using the results of Eqs. (13.245-13.316), the secondary  
 15 amino parameters in Eq. (15.52) are  $n_1 = 1$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  $C_{1o} = 0.75$ , and  $c_1 = 0.75$ . In secondary amines, the  $C2sp^3$  HO of the  $C-NH$ -bond MO has an energy of  $E(C, 2sp^3) = -15.56407 \text{ eV}$  (Eqs. (14.514-14.516)); Eq. (15.29) with  $s = 1$  and  $s = 2$ , Eq. (15.31), and Eqs. (15.19-15.20)) and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $N-H$   $H_2$ -  
 20 type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  of Eq. (15.52) for the  $N-H$ -bond MO given by Eq. (15.68) is

$$c_2(H \text{ to } 2^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383 \quad (15.117)$$

The  $C-N$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  
 25  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the



$C-N$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-N$ -bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ .

As given in the Continuous-Chain Alkanes ( $C_nH_{2n+2}$ ,  $n = 3, 4, 5, \dots, \infty$ ) section, each methylene group forms two single bonds, and the energy of each  $C2sp^3$  HO of each  $CH_2$  group alone is given by that in ethylene,  $-1.13379 \text{ eV}$  (Eq. (14.511)). In secondary amines, the  $N$  of the  $NH$  group also binds to two  $C2sp^3$  HOs and the corresponding  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of each  $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.13379 \text{ eV}$ . It is based on the energy match between the  $N$  of the  $NH$  group to the two  $C2sp^3$  HOs corresponding to the energy contributions to each of the two single bonds that are equivalent to those of independent methylene groups,  $-1.13379 \text{ eV}$  (Eq. (14.511)), where the  $N-H$  bond is also energy matched to the  $C-N$  bonds.  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.13379 \text{ eV}$ . It is based on the energy match between the  $N$  of the  $NH$  group to two  $C2sp^3$  HOs corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)), where the  $N-H$  bonds are also energy matched to the  $C-N$  bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of secondary amines are given in Tables 15.76, 15.77, and 15.78, respectively. As in the case of  $NH_2$  (Eq. (13.339)),  $C_{1o} = 2C_1$  rather than  $C_{1o} = C_1$  in Eq. (15.52) for the  $C-N$  bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.79-15.108) are given in Table 15.80.



Table 15.75. The symbols of functional groups of secondary amines.

Functional Group	Group Symbol
NH group	$NH$
C-N (methyl)	$C-N$ (i)
C-N (alkyl)	$C-N$ (ii)
$CH_3$ group	$C-H$ ( $CH_3$ )
$CH_2$ group	$C-H$ ( $CH_2$ )
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)



Table 15.76. The geometrical bond parameters of secondary amines and experimental values [1].

Parameter	NH Group	C-N (f) Group	C-N (ti) Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\sigma$ (a <sub>0</sub> )	1.26224	1.94862	1.94862	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (a <sub>0</sub> )	0.94811	1.39593	1.39593	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (Å)	1.00343	1.47739	1.47739	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.00 (dimethylamine)	1.455 (dimethylamine)	1.107 (C-H propane)	1.107 (C-H propane)	1.117 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
$h_c$ (a <sub>0</sub> )	0.83327	1.35960	1.35960	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$\epsilon$	0.75113	0.71637	0.71637	0.63380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.77. The MO to HO intercept geometrical bond parameters of secondary amines.  $R, R', R''$  are H or alkyl groups.  $E_f$  is  $E_f(\text{atom} - \text{atom}, \text{misp}^3, \text{AO})$ .

Bond	Atom	$E_f$ (eV) Bond 1	$E_f$ (eV) Bond 2	$E_f$ (eV) Bond 3	$E_f$ (eV) Bond 4	Final Total Energy $C^{2sp^3}$ (eV)	$r_{\text{final}}$ (a <sub>0</sub> )	$r_{\text{final}}$ (a <sub>0</sub> )	$E_{\text{Final}}$ (eV) Final	$E(C^{2sp^3})$ (eV) Final	$\theta^*$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
$H_2C-N(C_2H_5)-H$	N	-0.56690	-0.56690	0	0	-152.18259	0.93084	0.85252	-15.95954	-15.95954	118.18	61.82	64.40	0.54546	0.40264
$-H_2C-N(R_{\text{misp}})-H$	N	-0.56690	-0.56690	0	0	-152.18259	0.93084	0.85252	-15.95954	-15.95954	118.18	61.82	64.40	0.54546	0.40264
$H_2C-NH-C_2H_5$	C <sub>α</sub>	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	84.14	95.86	40.30	1.48625	0.09032
$H_2C-NH-C_2H_5$	N	-0.56690	-0.56690	0	0	-152.18259	0.93084	0.85252	-15.95954	-15.95954	80.95	99.05	38.26	1.53008	0.13415
$-H_2C-NH-C_2H_5$	C <sub>α</sub>	-0.56690	-0.92918	0	0	-153.11177	0.91771	0.83360	-16.32183	-16.13097	78.89	101.11	36.99	1.55650	0.16057
$-H_2C-NH-C_2H_5$	N	-0.56690	-0.56690	0	0	-152.18259	0.93084	0.85252	-15.95954	-15.95954	80.95	99.05	38.26	1.53008	0.13415
$C-H(CH_3)$	C	-0.92918	0	0	0	-152.44487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H(CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35466	0.29933
$C-H(CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_2C-C_2H_5CH_2-$	C <sub>α</sub>	-0.92918	0	0	0	-152.44487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_2C-C_2H_5CH_2-$	C <sub>β</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C-C_2H_5CH_2-$	C <sub>α</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C-C_2H_5CH_2-$	C <sub>β</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.93866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$HOOC-C_2H_5CH_2-$	C <sub>α</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$HOOC-C_2H_5CH_2-$	C <sub>β</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.93866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$HOOC-C_2H_5CH_2-$	C <sub>γ</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$HOOC-C_2H_5CH_2-$	C <sub>δ</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.93866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$HOOC-C_2H_5CH_2-$	C <sub>ε</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.93866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$HOOC-C_2H_5CH_2-$	C <sub>ζ</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.93866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.78. The energy parameters (eV) of functional groups of secondary amines.

Parameters	NH Group	C-N (i) Group	C-N (ii) Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	1	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	0.93613	1	1	1	1	1	1	1	1	1	1	1
$C_3$	0.75	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.93383	0.91140	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	1	0	0	0	1	1	0	0	0	1	1	0
$C_6$	1	2	2	1	1	1	2	2	2	2	2	2
$C_7$	1	0	0	3	2	1	0	0	0	0	0	0
$C_8$	0.75	1	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{9a}$	1	1	1	1	1	1	1	1	1	1	1	1
$V_1$ (eV)	-39.21967	-31.98456	-31.98456	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_2$ (eV)	14.30350	9.74677	9.74677	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T$ (eV)	15.53581	8.20698	8.20698	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_3$ (eV)	-7.76790	-4.10349	-4.10349	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{10}$ (eV)	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{10,10}$ (eV)	0	-1.13379	-1.13379	0	0	0	0	0	0	0	0	0
$E_{11}$ (eV)	-14.53414	-13.50110	-13.50110	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{12}$ (eV)	-31.63541	-31.63540	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{13}$ (eV)	0	-1.13379	-1.13379	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{14}$ (eV)	-31.63537	-32.76916	-32.76916	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ (10 <sup>6</sup> rad/s)	47.0696	15.1983	26.0778	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{15}$ (eV)	30.98202	10.00377	17.16484	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{16}$ (eV)	-0.34836	-0.20505	-0.26859	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{17}$ (eV)	0.40696	0.12944	0.11159	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{18}$ (eV)	-0.14488	-0.14033	-0.21280	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{19}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{20}$ (eV)	-31.78025	-32.90949	-32.98196	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{21}$ (eV)	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{22}$ (eV)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{23}$ (eV)	3.50582	3.63971	3.71218	12.49186	7.83016	3.32601	4.32754	4.29921	3.97598	4.17951	3.62128	3.91734

Table 15.79. The total bond energies of secondary amines calculated using the functional group composition and the energies of Table 15.78 compared to the experimental values [3].

Formula	Name	NH Group	C-N (i) Group	C-N (ii) Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> N	Dimethylamine	1	2	0	2	0	0	0	0	0	0	0	0	35.76855	35.765	-0.00012
C <sub>2</sub> H <sub>5</sub> N	Diethylamine	1	0	2	2	2	0	0	0	0	0	0	0	60.22910	60.211	-0.00030
C <sub>3</sub> H <sub>7</sub> N	Dipropylamine	1	0	2	2	4	0	0	0	0	0	0	0	84.54770	84.558	0.00016
C <sub>4</sub> H <sub>9</sub> N	Diisopropylamine	1	0	2	4	0	4	0	0	0	0	0	0	84.74648	84.846	0.00117
C <sub>5</sub> H <sub>11</sub> N	Dibutylamine	1	0	2	2	6	0	0	0	0	0	0	0	108.86010	108.872	0.00011
C <sub>6</sub> H <sub>13</sub> N	Diisobutylamine	1	0	2	4	2	2	6	0	0	0	0	0	109.00322	109.106	0.00092







TERTIARY AMINES ( $C_nH_{2n+3}N$ ,  $n = 3, 4, 5 \dots \infty$ )

The tertiary amines,  $C_nH_{2n+3}N$ , have three  $C-N$  bonds to methyl or alkyl groups wherein  $C-N$  comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise  
 5 methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl,  
 10 and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The  $C-N$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy.  
 15 In tertiary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-N$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-N$ -bond MO given by Eq. (15.116) is  $c_2(C2sp^3 \text{ HO to N}) = 0.91140$ .

20 As given in the Continuous-Chain Alkanes ( $C_nH_{2n+2}$ ,  $n = 3, 4, 5 \dots \infty$ ) section, the energy of each  $C2sp^3$  HO must be a linear combination of that of the  $CH_3$  and  $CH_2$  groups that serve as basis elements. Each  $CH_3$  forms one  $C-C$  bond, and each  $CH_2$  group forms two. Thus, the energy of each  $C2sp^3$  HO of each  $CH_3$  and  $CH_2$  group alone is given by that in ethane,  $-0.72457 \text{ eV}$  (Eq. (14.151)), and ethylene,  $-1.13379 \text{ eV}$  (Eq. (14.511)), respectively. In order  
 25 to match the energy of the component HOs and MOs for the entire molecule, the energy  $E_{T_{alkane}}(C-C, 2sp^3)$  given as a linear combination of these basis elements is  $-0.92918 \text{ eV}$  (Eq. (14.513)). In tertiary amines, the  $N$  binds to three  $C2sp^3$  HOs and the corresponding  $E_T(atom - atom, msp^3 \cdot AO)$  of each  $C-N$ -bond MO in Eq. (15.52) due to the charge donation



from the *C* and *N* atoms to the MO is  $-0.92918\text{ eV}$ . It comprises a linear combination of the energy for a primary amine,  $-0.72457\text{ eV}$  and a secondary amine,  $-1.13379\text{ eV}$ .

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and  
5 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.79-15.108) are given in Table 15.86.



Table 15.81. The symbols of functional groups of tertiary amines.

Functional Group	Group Symbol
C-N	C-N
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C'-C' (a)
CC bond (iso-C)	C'-C' (b)
CC bond (tert-C)	C'-C' (c)
CC (iso to iso-C)	C'-C' (d)
CC (t to t-C)	C'-C' (e)
CC (t to iso-C)	C'-C' (f)

Table 15.82. The geometrical bond parameters of tertiary amines and experimental values [1].

Parameter	C-N Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C'-C' (a) Group	C'-C' (b) Group	C'-C' (c) Group	C'-C' (d) Group	C'-C' (e) Group	C'-C' (f) Group
$\alpha$ (°)	1.96313	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$\alpha'$ (°)	1.40112	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length, 2c' (Å)	1.48288	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.458 (trimethylamine)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c$ (°)	1.37505	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.71372	0.63580	0.63159	0.62095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.83. The MO to HO intercept geometrical bond parameters of tertiary amines.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_r(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{Orbital}}$ (eV) Final	$E(C2sp^3)$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$N-(C_2H_5)_3$	$C_u$	-0.46459		0	0	-152.08028	0.91771	-15.28034	-15.09948	83.37	96.63	40.00	1.50383	0.10271
$N-(C_2H_5)_3$	$N$	-0.46459	-0.46459	-0.46459	0	0	0.93084	-16.21953		78.02	101.98	36.64	1.57525	0.17413
$N-(C_2H_5)_3$	$C_u$	-0.46459	-0.92918	0	0	-153.00946	0.91771	-16.21953	-16.02866	78.02	101.98	36.64	1.57525	0.17413
$N-(C_2H_5)_3$	$N$	-0.46459	-0.46459	-0.46459	0	0	0.93084	-16.21953		78.02	101.98	36.64	1.57525	0.17413
$C-H (CH_3)$	$C$	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	-15.56407	77.49	102.51	41.48	1.25564	0.18708
$C-H (CH_3)$	$C$	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H (CH)$	$C$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37226
$H_3C-C_3H_7$	$C_u$	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C-C_3H_7$	$C_h$	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C-C_3H_7$	$C_h$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C-C_3H_7$	$C_h$	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50270
$isoC-C_3H_7$	$C_h$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC-C_3H_7$	$C_h$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC-C_3H_7$	$C_h$	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC-C_3H_7$	$C_h$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.84. The energy parameters (eV) of functional groups of tertiary amines.

Parameters	C-N Group	(H <sub>3</sub> ) Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1
$C_4$	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	1	1	0	0	0	1	1	0
$C_6$	2	1	1	1	2	2	2	2	2	2
$C_7$	0	3	2	1	0	0	0	0	0	0
$C_{10}$	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{11}$	1	1	1	1	1	1	1	1	1	1
$V_e$ (eV)	-31.67393	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
$V_p$ (eV)	9.71067	38.92728	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
$T$ (eV)	8.06719	32.53914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
$V_u$ (eV)	-4.03359	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
$E_{12,12}$ (eV)	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{12,12}$ (eV)	0	0	0	0	0	0	0	0	0	0
$E_{12,12}$ (eV)	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{12,12}$ (eV)	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$E_{12,12}$ (eV)	-0.92918	0	0	0	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836
$E_{12,12}$ (eV)	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\omega$ (10 <sup>5</sup> rad/s)	18.1298	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.43699	9.43699
$E_{12}$ (eV)	11.93333	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
$E_{12}$ (eV)	-0.22255	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515
$E_{12}$ (eV)	0.12944	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
$E_{12}$ (eV)	[23]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[2]	[4]	[5]	[2]	[2]	[2]
$E_{12}$ (eV)	-0.15783	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10359	-0.10359
$E_{12}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{12}$ (eV)	-32.72238	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$E_{12}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{12}$ (eV)	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{12}$ (eV)	3.45260	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.85. The total bond energies of tertiary amines calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

Formula	Name	C-N Group	(H <sub>3</sub> ) Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>9</sub> N	Trimethylamine	3	3	0	0	0	0	0	0	0	0	47.83338	47.761	-0.00152
C <sub>6</sub> H <sub>15</sub> N	Triethylamine	3	3	3	0	3	0	0	0	0	0	84.30648	84.316	0.00012
C <sub>9</sub> H <sub>21</sub> N	Tripropylamine	3	3	6	0	6	0	0	0	0	0	120.77958	120.864	0.00070



Table 15.86. The bond angle parameters of tertiary amines and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

Atoms at Angle	$2c'$ Bond 1 ( $a_0$ )	$2c'$ Bond 2 ( $a_0$ )	$2c'$ Terminal Atoms ( $a_0$ )	$E_{\text{calculation}}$ or $E$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{calculation}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c'_2$	$E_T$ (eV)	$\theta_i$ ( $^\circ$ )	$\theta_j$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle \text{NC}$	2.80224	2.80224	4.6043	-17.14871	I	-17.14871	6	0.79340	0.79340	I	I	I	0.79340	-1.85836			110.48	110.9 (trimethylamine)
Methylene $\angle \text{HC}_\alpha \text{H}$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	I	I	I	0.75	1.15796	0			103.44	107 (dimethylamine)
$\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$																		112 (propane)
$\angle \text{C}_\alpha \text{C}_\beta \text{H}$															69.51		110.49	113.8 (butane)
Methyl $\angle \text{HC}_\alpha \text{H}$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	I	I	I	0.75	1.15796	0			110.49	110.8 (isobutane)
$\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$															69.51			111.0 (butane)
$\angle \text{C}_\alpha \text{C}_\beta \text{H}$																		111.4 (isobutane)
$\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$ iso $\text{C}_\alpha$	2.91547	2.91547	4.7958	-16.68412	25	$\text{C}_\alpha$	25	0.81549	0.81549	I	I	I	0.81549	-1.85836			110.67	110.8 (isobutane)
$\angle \text{C}_\alpha \text{C}_\beta \text{H}$ iso $\text{C}_\alpha$	2.91547	2.11323	4.1633	-15.55033	5	$\text{C}_\alpha$	1	0.87495	0.91771	0.75	I	0.75	1.04887	0			110.76	
$\angle \text{C}_\alpha \text{C}_\beta \text{H}$ iso $\text{C}_\alpha$	2.91547	2.09711	4.1633	-15.55033	5	$\text{C}_\alpha$	1	0.87495	0.91771	0.75	I	0.75	1.04887	0			111.27	111.4 (isobutane)
$\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$ test $\text{C}_\alpha$	2.90327	2.90327	4.7958	-15.55033	5	$\text{C}_\alpha$	1	0.87495	0.91771	0.75	I	0.75	1.04887	-1.85836			111.27	111.4 (isobutane)
$\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$															72.50		107.50	



ALDEHYDES ( $C_nH_{2n}O$ ,  $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl aldehydes,  $C_nH_{2n}O$ , each have a  $HC=O$  moiety that comprises a  $C=O$  functional group and a  $CH$  functional group. The single bond of carbon to the carbonyl carbon atom,  $C-C(O)H$ , is a functional group. In addition to the  $C=O$  functional group, formaldehyde comprises a  $CH_2$  functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The  $CH$  functional group was solved in the Hydrogen Carbide ( $CH$ ) section except that  $E_{mag}$  is not subtracted since unpaired electrons are not created with fragmentation of the functional group of aldehydes. The  $CH_2$  functional group of formaldehyde is solved in the Dihydrogen Carbide ( $CH_2$ ) section except that the energy of each  $C-H$  MO is matched to the initial energy of the  $C2sp^3$  HO (Eq. (15.25)). The  $C=O$  and  $C-C(O)H$  groups are solved by hybridizing the  $2s$  and  $2p$  AOs of each  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $O$  AO or between two  $C2sp^3$  HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of the  $C=O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C=O$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ . The unpaired electrons created by bond breakage of the double  $C=O$  bond requires that two times



the  $O2p$  AO magnetic energy  $E_{mag}$  (Eq. (15.60)) be subtracted from the total energy to give  $E_D(\text{Group})$  (eV) for  $C = O$ .

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C = O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-2.69893$  eV which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the  $C$  atom and the pair of AO electrons of the  $O$  atom. It is given as a linear combination of the energy contributions corresponding to a double bond,  $-1.13379$  eV (Eq. (14.247)), and a triple bond,  $-1.56513$  eV (Eq. (14.342)). The triple bond contribution includes the  $C2sp^3$  HO electron of the  $C - H$  bond in addition to the pair involved directly in the double bond with  $O$ .

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C - C(O)H$  group is equivalent to that of an alkane,  $-1.85836$  eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the aldehyde. In order to match energy between the groups bonded to the  $C = O$ , electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing,  $C_{1o} = 2C_1$  rather than  $C_{1o} = C_1$  in Eq. (15.52) for the  $C - C(O)H$  bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.79-15.108) are given in Table 15.92.



Table 15.87. The symbols of functional groups of alkyl aldehydes.

Functional Group	Group Symbol
CH <sub>2</sub> (formaldehyde) group	$C - H (CH_2)$ (i)
CH (aldehyde) group	$CH$ (i)
C=O	$C = O$ (i)
C-C(O)H	$C - C(O)H$
CH <sub>3</sub> group	$C - H (CH_3)$
CH <sub>2</sub> (alkyl) group	$C - H (CH_2)$ (ii)
CH (alkyl)	$C - H$ (ii)
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 15.88. The geometrical bond parameters of alkyl aldehydes and experimental values [1].

Parameter	$C-H$ (i)	$C=O$ Group	$C-C(O)H$ Group	$C-H$ (CH <sub>2</sub> ) Group	$C-H$ (CH <sub>3</sub> ) Group	$C-H$ (CH <sub>2</sub> ) Group	$C-H$ (i)	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a$ (Å)	1.64010	1.29907	2.04740	1.64920	1.67122	1.67465	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.04566	1.13977	1.43087	1.04856	1.05553	1.05661	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length	1.10668	1.20628	1.51437	1.10974	1.11713	1.11827	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
$2c'$ (Å)	1.116 (formaldehyde)	1.208 (formaldehyde)	1.515 (acetaldehyde)	1.117 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
Exp. Bond Length (Å)	1.116 (formaldehyde)	1.210 (acetaldehyde)	1.515 (acetaldehyde)	1.117 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.122 (isobutane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)
$h, c$ (Å)	1.26354	0.62331	1.46439	1.27295	1.29569	1.29924	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.63756	0.87737	0.69887	0.63580	0.63159	0.63095	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.89. The MO to HO intercept geometrical bond parameters of alkyl aldehydes.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T$  (atom-atom, nsp<sup>3</sup> AO).

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Energy (eV)	$r_{final}$ (Å)	$r_{initial}$ (Å)	$E_{centrals}$ (eV) Final	$E(C2sp^3)$ (eV) Final	$\theta'$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (Å)	$d_2$ (Å)
$H-C(O)-H$ (CH <sub>2</sub> ) (i)	C'	-1.34946	0	0	0	-152.96515	0.91771	0.84115	-16.17521	-15.98435	75.72	104.28	40.18	1.25314	0.20748
$-C(H_2C_2O)-H$ (CH) (i)	C''	-1.34946	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	64.95	115.05	33.69	1.39345	0.33684
$H_2C=O$	O	-1.34946	0	0	0	1.00000	0.84115	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$-CH_2CH_2-C(H)(O)$	C''	-1.34946	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	137.27	42.73	66.31	0.52193	0.61784
$H_2C_2-C(H)(O)$	C''	-1.34946	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	137.27	42.73	66.31	0.52193	0.61784
$-CH_2CH_2-C(H)(O)$	C''	-0.92918	-0.92918	0	0	-153.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$C'-H$ (CH <sub>2</sub> ) (ii)	C'	-0.92918	0	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H$ (CH <sub>2</sub> ) (iii)	C'	-0.92918	-0.92918	0	0	-153.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H$ (CH) (iii)	C'	-0.92918	-0.92918	-0.92918	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$H_2C_2-C(H_2C_2O)$	C''	-0.92918	0	0	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37226
$H_2C_2-C(H_2C_2O)$	C''	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$C'-C$ (a)	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_2-C(H_2C_2O)$	C''	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2-C(H_2C_2O)$	C''	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$C'-C$ (b)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2-C(H_2C_2O)$	C''	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$R-H_2C_2-C(H_2C_2O)$	C''	-0.72457	-0.72457	-0.72457	0	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$R-H_2C_2-C(H_2C_2O)$	C''	-0.72457	-0.72457	-0.72457	0	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$R-H_2C_2-C(H_2C_2O)$	C''	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$R-H_2C_2-C(H_2C_2O)$	C''	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.90. The energy parameters (eV) of functional groups of alkyl aldehydes.

Parameters	$CH_2$ (i)	$CH$ (i)	$C=O$ Group	$C-C(OH)$ Group	$CH_3$ Group	$CH_2$ (ii)	$C-H$ (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)
$n_1$	2	1	2	1	3	2	1	1	1	1	1	1	1
$n_2$	1	0	0	0	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.75	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.91771	0.91771	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	1	0	2	0	0	1	1	0	0	0	1	1	0
$C_6$	1	1	4	2	1	1	1	2	2	2	2	2	2
$C_7$	2	1	0	0	3	2	1	0	0	0	0	0	0
$C_{10}$	0.75	0.75	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{20}$	1	1	1	1	1	1	1	1	1	1	1	1	1
$V_e$ (eV)	-72.03287	-35.12015	-111.25473	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-29.10112	-29.10112
$V_p$ (eV)	26.02344	12.87680	23.87467	9.50874	38.92728	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.37273	9.37273
$T$ (eV)	21.95990	10.48582	42.82081	7.37432	32.53914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.90500	6.90500
$V_{\pi}$ (eV)	-10.97995	-5.24291	-21.41040	-3.68716	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.45250	-3.45250
$E_{Lip}$ (eV)	-14.63489	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.35946	-15.35946
$\Delta E_{Lip}$ (eV)	0	0	-2.69893	0	0	0	0	0	0	0	0	0	0
$E_{\pi}^*$ (eV)	-14.63489	-14.63489	2.69893	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.35946	-15.35946
$E_{\pi}^*$ (eV)	-49.66493	-31.63537	-65.96966	-33.49373	-67.69450	-49.66493	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63535	-31.63535
$F_{\pi}$ (atom - atom, msp, AC) (eV)	0	0	-2.69893	-1.85836	0	0	0	-1.85836	-1.85836	-1.85836	-1.85836	-1.44915	-1.44915
$E_{\pi}^*$ (eV)	-49.66493	-31.63537	-65.96966	-33.49373	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^{15}$ rad/s)	25.2077	24.1759	59.4034	23.2291	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.55643	9.55643
$E_{\pi}^*$ (eV)	16.59214	15.91299	39.10034	15.35563	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.29021	6.29021
$E_{\pi}^*$ (eV)	-0.23493	-0.24966	-0.40804	-0.25966	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16416	-0.16416
$E_{\pi}^*$ (eV)	0.35352	0.35352	0.21077	0.13800	0.35352	0.35352	0.35352	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
$E_{\pi}^*$ (eV)	-0.07727	-0.07200	-0.30266	-0.19066	-0.22757	-0.14502	-0.07200	-0.10359	-0.07326	-0.07326	-0.10359	-0.10260	-0.10260
$E_{\pi}^*$ (eV)	0.14803	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\pi}^*$ (eV)	-49.81948	-31.70737	-66.57498	-33.68439	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.49373	-33.59732	-33.18712	-33.18712
$E_{\pi}^*$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\pi}^*$ (eV)	-13.59844	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\pi}^*$ (eV)	7.83968	3.47404	7.80660	4.41461	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.91. The total bond energies calculated using the functional group composition and the energies of Table 15.90 compared to the experimental values [3].

Formula	Name															
	$CH_2$ (i)	$CH$ (i)	$C=O$	$C-C(O)H$	$CH_3$	$CH_2$ (ii)	$CH$ (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$CH_2O$	1	0	1	0	0	0	0	0	0	0	0	0	0	15.655	15.655	0.00056
Formaldehyde	0	1	1	1	1	0	0	0	0	0	0	0	0	28.18711	28.188	0.00039
$CH_3O$	0	1	1	1	1	1	0	0	0	0	0	0	0	40.34481	40.345	0.00000
Propanal	0	1	1	1	1	1	0	0	0	0	0	0	0	52.50251	52.491	-0.00022
$CH_4O$	0	1	1	1	2	0	0	2	0	0	0	0	0	64.66021	64.682	0.00034
Butanal	0	1	1	1	2	0	0	0	0	0	0	0	0	76.81791	76.840	0.00029
$CH_5O$	0	1	1	1	3	0	0	3	0	0	0	0	0	88.97561	88.942	-0.00038
Isobutanol	0	1	1	1	3	0	0	0	0	0	0	0	0	101.13331	101.179	0.00045
$CH_6O$	0	1	1	1	4	0	0	4	0	0	0	0	0	113.29101	113.337	0.00043
Pentanol	0	1	1	1	4	0	0	0	0	0	0	0	0	125.44871	125.494	0.00037
$CH_7O$	0	1	1	1	5	0	0	5	0	0	0	0	0	137.60641	137.652	0.00034
Hexanol	0	1	1	1	5	0	0	0	0	0	0	0	0	149.76411	149.810	0.00032
$CH_8O$	0	1	1	1	6	0	0	6	0	0	0	0	0	161.92181	161.967	0.00029
Heptanol	0	1	1	1	6	0	0	0	0	0	0	0	0	174.07951	174.125	0.00026
$CH_9O$	0	1	1	1	7	0	0	7	0	0	0	0	0	186.23721	186.283	0.00025
Octanol	0	1	1	1	7	0	0	0	0	0	0	0	0	198.39491	198.440	0.00024
$CH_{10}O$	0	1	1	1	8	0	0	8	0	0	0	0	0	210.55261	210.598	0.00022
2-Ethylhexanol	0	1	1	1	2	1	1	3	0	0	0	0	0	222.71031	222.756	0.00021



Table 15.92. The bond angle parameters of alkyl aldehydes and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, mp^2, AO)$ .

Atom of Angle	$2c_1'$ Bond 1 ( $\theta_1$ )	$2c_2'$ Bond 2 ( $\theta_2$ )	$2c'$ Terminal Atom ( $\theta_0$ )	$E_{\text{Terminal}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{Terminal}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_1$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$\phi_1$	$\phi_2$	$E_T$ (eV)	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle HC_1H$ ( $C_1H_4(O)$ (i))	2.09132	2.09132	3.5637	-16.39089	18	H	H	0.83008	1	1	1	0.75	1.20470	0			116.87	116.5 (formaldehyde)
$\angle C_1C_2H$ $RC_1(H)=O$	2.86175	2.11323	4.2269	-15.75493	7	$C_b$	1	0.86359	0.91771	0.75	1	0.75	1.06267	0			115.52	115.3 (acetaldehyde)
$\angle C_1C_2O$ Methylene	2.86175	2.79354	4.5826	-16.68412	25	$C_b$	0	0.81549	0.83295 (Eq. 15.114)	1	1	1	0.83472	-1.65376			125.70	124.1 (acetaldehyde)
$\angle HC_1H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0			108.44	107 (propane)
$\angle C_1C_2C_3$															69.51		110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_1C_2H$															69.51		110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_1H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0			109.50	109.8 (acetaldehyde)
$\angle C_1C_2C_3$															70.56		109.44	
$\angle C_1C_2H$															70.56		109.44	
$\angle C_1C_2C_3$ iso $C_b$	2.91547	2.91547	4.7958	-16.68412	25	$C_b$	25	0.81549	0.81549	1	1	1	0.81549	-1.83836			110.67	110.8 (isobutane)
$\angle C_1C_2H$ iso $C_b$	2.91547	2.11323	4.1633	-15.55033	5	$C_b$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0			110.76	
$\angle C_1C_2H$ iso $C_b$	2.91547	2.09711	4.1633	-15.55033	3	$C_b$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0			111.27	111.4 (isobutane)
$\angle C_1C_2C_3$ tert $C_b$	2.90327	2.90327	4.7958	-15.55033	5	$C_b$	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.83836			111.27	111.4 (isobutane)
$\angle C_1C_2C_3$															72.50		107.50	



KETONES ( $C_nH_{2n}O$ ,  $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl ketones,  $C_nH_{2n}O$ , each have a  $C=O$  moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The  $C=O$  and  $C-C(O)$  groups are solved by hybridizing the  $2s$  and  $2p$  AOs of each  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $O$  AO or between two  $C2sp^3$  HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of the  $C=O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C=O$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ . The unpaired electrons created by bond breakage of the double  $C=O$  bond requires that two times the  $O2p$  AO magnetic energy  $E_{mag}$  (Eq. (15.60)) be subtracted from the total energy to give  $E_D(\text{Group})$  (eV) for  $C=O$ .

As in the case with aldehydes,  $E_T(\text{atom-atom}, msp^3.AO)$  of the  $C=O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-2.69893 \text{ eV}$  which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the  $C$  atom and the pair of AO electrons of the  $O$  atom. It is given as a linear combination of



the energy contributions corresponding to a double bond,  $-1.13379 \text{ eV}$  (Eq. (14.247)), and a triple bond,  $-1.56513 \text{ eV}$  (Eq. (14.342)). The triple bond contribution includes the  $C2sp^3$  HO electron of the  $C-C(O)$  bond in addition to the pair involved directly in the double bond with  $O$ . Consequently,  $E_T(\text{atom-atom}, msp^3.AO)$  of the  $C-C(O)$ -bond MO is  $-1.44915 \text{ eV}$ ,  
 5 corresponding to the energy contributions of the two  $C2sp^3$  HOs to the single bond that are equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)). Since there are two  $C-C(O)$  bonds in ketones versus one in aldehydes,  $C_{1o} = C_1$  in Eq. (15.52) for each  $C-C(O)$  ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The  
 10 geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.55)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by  
 15 bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl ketones determined using Eqs. (15.79-15.108) are given in Table 15.98.

Table 15.93. The symbols of functional groups of alkyl ketones.

Functional Group	Group Symbol
$C=O$	$C=O$
$C-C(O)$	$C-C(O)$
$CH_3$ group	$C-H (CH_3)$
$CH_2$ group	$C-H (CH_2)$
$CH$	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)



Table 15.95. The MO to HO intercept geometrical bond parameters of alkyl ketones.  $R, R', R''$  are  $H$  or alkyl groups.  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C_{2sp}^i$ (eV)	$r_{ind}$ ( $a_0$ )	$r_{rad}$ ( $a_0$ )	$E_{extind}$ (eV) Final	$E(C_{2sp}^j)$ (eV) Final	$\theta^i$ ( $^\circ$ )	$\theta_i$ ( $^\circ$ )	$\theta_s$ ( $^\circ$ )	$d_i$ ( $a_0$ )	$d_s$ ( $a_0$ )
$R^+C_1H_2(RC_6H_5)_2C_7=O$	O	-1.34046	0	0	0	1.00000	0.84115	0.84115	-16.17521	136.09	136.09	43.91	63.72	0.53955	0.60595
$R^+C_1H_2(RC_6H_5)_2C_7=O$	C <sub>6</sub>	-1.34046	-0.72458	-0.72458	0	0.91771	0.77199	0.77199	-17.62437	133.02	133.02	46.98	61.86	0.61878	0.52672
$H_1C_1-C_6(O)(R^+)$	C <sub>6</sub>	-0.72458	0	0	0	0.91771	0.87495	0.87495	-15.53033	153.62	153.62	106.38	34.98	1.07762	0.246675
$RH_2C_7-H_2C_6-C_7(O)(R^+)$	C <sub>6</sub>	-0.72458	-0.92918	0	0	0.91771	0.82562	0.82562	-16.47951	112.60	112.60	112.60	31.36	1.74821	0.31734
$C^+-H(CH_3)$	C <sup>+</sup>	-0.92918	0	0	0	0.91771	0.86359	0.86359	-15.75493	110.51	110.51	102.51	41.48	1.23564	0.18708
$C^+-H(CH_3)$	C <sup>+</sup>	-0.92918	-0.92918	0	0	0.91771	0.81549	0.81549	-16.68412	116.82	116.82	111.53	35.84	1.35486	0.29933
$C^+-H(CH_3)$	C <sup>+</sup>	-0.92918	-0.92918	-0.92918	0	0.91771	0.77247	0.77247	-17.61330	118.90	118.90	118.90	31.37	1.42988	0.37326
$H_1C_1C_6H_2CH_2-$ (C-C (a))	C <sub>6</sub>	-0.92918	0	0	0	0.91771	0.86359	0.86359	-15.75493	116.18	116.18	116.18	30.08	1.83879	0.38106
$H_1C_1C_6H_2CH_2-$ (C-C (a))	C <sub>6</sub>	-0.92918	-0.92918	0	0	0.91771	0.81549	0.81549	-16.68412	123.59	123.59	123.59	26.06	1.90890	0.45117
$R-H_1C_1C_6(H_1C_1-C-R^+)HCCH_2-$ (C-C (b))	C <sub>6</sub>	-0.92918	-0.92918	-0.92918	0	0.91771	0.77247	0.77247	-17.61330	131.70	131.70	131.70	21.90	1.97162	0.51388
$R-H_1C_1C_6(R^+-H_1C_1C_6)(C_6(R^+-H_1C_1C_6)(C_6H_2-$ (C-C (c))	C <sub>6</sub>	-0.92918	-0.72457	-0.72457	-0.72457	0.91771	0.73889	0.73889	-17.92866	48.21	48.21	131.79	21.74	1.95734	0.50570
$isoC_6C_6(H_1C_1-C-R^+)HCCH_2-$ (C-C (d))	C <sub>6</sub>	-0.92918	-0.92918	-0.92918	0	0.91771	0.77247	0.77247	-17.61330	48.30	48.30	131.70	21.90	1.97162	0.51388
$isoC_6C_6(R^+-H_1C_1C_6)(C_6(R^+-H_1C_1C_6)(CH_2-$ (C-C (e))	C <sub>6</sub>	-0.72457	-0.72457	-0.72457	-0.72457	0.91771	0.76765	0.76765	-17.92866	50.04	50.04	129.96	22.66	1.94462	0.49298
$isoC_6C_6(H_1C_1-C-R^+)HCCH_2-$ (C-C (f))	C <sub>6</sub>	-0.72457	-0.92918	-0.92918	0	0.91771	0.78155	0.78155	-17.40869	52.78	52.78	127.22	24.04	1.92443	0.47279
$isoC_6C_6(R^+-H_1C_1C_6)(C_6(R^+-H_1C_1C_6)(CH_2-$ (C-C (f))	C <sub>6</sub>	-0.72457	-0.72457	-0.72457	-0.72457	0.91771	0.76765	0.76765	-17.92866	50.04	50.04	129.96	22.66	1.94462	0.49298



Table 15.96. The energy parameters (eV) of functional groups of alkyl ketones.

Parameters	C=O Group	C-C(O) Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	2	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0
$\eta_4$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_1$	1	1	1	1	1	1	1	1	1	1	1
$\zeta_2$	1	1	1	1	1	1	1	1	1	1	1
$\zeta_3$	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\zeta_4$	2	0	0	1	1	0	0	0	1	1	0
$\zeta_5$	4	2	1	1	1	2	2	2	2	2	2
$\zeta_6$	0	0	3	2	1	0	0	0	0	0	0
$\zeta_{in}$	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_{3a}$	1	1	1	1	1	1	1	1	1	1	1
$V_e$ (eV)	-109.17602	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p$ (eV)	23.75521	9.50874	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T$ (eV)	41.60126	7.37432	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_n$ (eV)	-20.80063	-3.68716	-16.26937	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(x\text{ in})$ (eV)	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_{2,30}}$ (eV)	-1.34946	0	0	0	0	0	0	0	0	0	0
$E_T$ (eV)	1.34946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(x\text{ in})$ (eV)	-63.27071	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(\text{atom} - \text{atom}, \text{msq}, \text{AO})$ (eV)	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(x\text{ in})$ (eV)	-65.96966	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^6 \text{ rad/s}$ )	57.0928	16.4962	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K$ (eV)	37.57947	10.83807	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_n$ (eV)	-0.40003	-0.21568	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{Kw}$ (eV)	0.21462	0.14655	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{Kw}$ (eV)	[27]	[28]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[2]	[4]	[5]	[2]	[2]	[2]
$E_{Kw}$ (eV)	-0.29272	-0.14240	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{Kw}$ (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(x\text{ in})$ (eV)	-66.55510	-33.22692	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24376	-33.59732	-33.18712	-33.18712
$E_{Kw}(x\text{ in})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{Kw}(x\text{ in})$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{Kw}(x\text{ in})$ (eV)	7.78672	3.95714	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734



Table 15.97. The total bond energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values [3]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_b$  ( $eV$ ) values based on composition is given by (15.57).

Formula	Name	C=O Group	C-C(O) Group	C <sub>1</sub> H <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	E <sub>mag</sub>	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>4</sub> O	Acetone	1	2	2	0	0	0	0	0	0	0	0	0	40.672	40.672	-0.00031
C <sub>4</sub> H <sub>8</sub> O	2-Butanone	1	2	2	1	0	1	0	0	0	0	0	0	52.842	52.84	-0.00005
C <sub>6</sub> H <sub>12</sub> O	3-Pentanone	1	2	2	2	0	2	0	0	0	0	0	0	65.00012	64.997	-0.00005
C <sub>8</sub> H <sub>16</sub> O	3-Methyl-2-butanone	1	2	3	0	1	0	2	0	0	0	0	0	65.00012	64.997	-0.00005
C <sub>8</sub> H <sub>16</sub> O	2-Hexanone	1	2	2	2	0	3	0	0	0	0	0	0	77.15782	77.152	-0.00008
C <sub>8</sub> H <sub>16</sub> O	3-Hexanone	1	2	2	3	0	3	0	0	0	0	0	0	77.15782	77.138	-0.00025
C <sub>8</sub> H <sub>16</sub> O	2-Heptanone	1	2	3	1	1	1	2	0	0	0	0	-2	77.25871	77.225	-0.00043
C <sub>8</sub> H <sub>16</sub> O	3,3-Dimethyl-2-butanone	1	2	4	0	0	0	0	3	0	0	0	-2	77.25871	77.273	-0.00032
C <sub>8</sub> H <sub>16</sub> O	4-Heptanone	1	2	2	4	0	4	0	0	0	0	0	0	89.31552	89.287	-0.00032
C <sub>8</sub> H <sub>16</sub> O	2,2-Dimethyl-3-pentanone	1	2	4	1	0	1	0	0	0	0	0	-2	89.31552	89.299	-0.00018
C <sub>8</sub> H <sub>16</sub> O	2,4-Dimethyl-3-pentanone	1	2	4	0	2	0	4	0	0	0	0	0	89.45202	89.453	0.00007
C <sub>8</sub> H <sub>16</sub> O	2,2,4-Trimethyl-3-pentanone	1	2	5	0	0	0	2	0	0	0	0	0	89.51730	89.434	-0.00093
C <sub>8</sub> H <sub>16</sub> O	2-Nonanone	1	2	2	6	0	6	0	0	0	0	0	-2	101.71061	101.660	-0.00049
C <sub>8</sub> H <sub>16</sub> O	5-Nonanone	1	2	2	6	0	6	0	0	0	0	0	0	113.63092	113.632	0.00001
C <sub>8</sub> H <sub>16</sub> O	2,6-Dimethyl-4-heptanone	1	2	4	2	2	0	6	0	0	0	0	0	113.63092	113.675	0.00039
													0	113.77604	113.807	0.00027

Table 15.98. The bond angle parameters of alkyl ketones and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_i$  is  $E_i$  (atom-atom, nisp, AO).

Atoms of Angle	$2\alpha'$ Bond 1 ( $a_0$ )	$2\alpha'$ Bond 2 ( $a_0$ )	$2\alpha'$ Terminal Atom ( $a_0$ )	$E_i$ Terminal Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$F_i$ Coordinate Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_i$ Atom 1	$c_i$ Atom 2	$C_1$	$C_2$	$c_1$	$c'_1$	$E_T$ (eV)	$\theta_i$ ( $^\circ$ )	$\theta_i$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )	
$ZC_2C_2OC_c$	2.86175	2.86175	4.8477	-16.68412 $C'_h$	25	-16.68412 $C'_e$	25	0.81549	0.81549	1	1	1	0.81549	-1.85836			115.77	116.0 (acetone)	
$ZC_2C_2C_3(O)$	2.91547	2.86175	4.8374	-16.68412 $C'_d$	25	-16.68412 $C'_e$	25	0.81549	0.81549	1	1	1	0.81549	-1.85836			113.71	113.5 (2-butanone)	
$ZC_2C_2O$	2.86175	2.29100	4.5166	-15.55033	5	-13.61806	O (Eq. 13.114)	0.87495	0.85395	1	1	1	0.86445	-1.44915			122.07	121.9 (2-butanone)	
Methyl: $ZHC_2H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0			108.44	107 (propane)	
																	112		
$ZC_2C_2C'_e$															69.51			110.49	113.8 (butane)
																		110.8 (isobutane)	
$ZC_2C_2H$																		111.0 (butane)	
															69.51			111.4 (isobutane)	
Methyl $ZHC_2H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0			105.50	108.5 (acetone)	
$ZC_2C_2C'_e$																		109.44	
$ZC_2C_2H$																		109.44	
$ZC_2C_2C'_e$																			
$ZC_2C_2C'_e$ iso $C'_e$	2.91547	2.91547	4.7958	-16.68412 $C'_h$	25	-16.68412 $C'_e$	25	0.81549	0.81549	1	1	1	0.81549	-1.85836			110.67	110.8 (isobutane)	
$ZC_2C_2H$ iso $C'_e$	2.91547	2.11323	4.1633	-15.55033 $C'_d$	5	-14.82575 $C'_e$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0			110.76		
$ZC_2C_2H$ iso $C'_d$	2.91547	2.09711	4.1633	-15.55033 $C'_h$	5	-14.82575 $C'_e$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0			111.27	111.4 (isobutane)	
$ZC_2C_2C'_e$ tert $C'_e$	2.90327	2.90327	4.7958	-15.55033 $C'_h$	5	-14.82575 $C'_e$	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836			111.27	111.4 (isobutane)	
$ZC_2C_2C'_e$																	107.50		



# CARBOXYLIC ACIDS ( $C_nH_{2n}O_2$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl carboxylic acids,  $C_nH_{2n}O_2$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. Formic acid has a  $HC=O$  moiety that comprises a more stable  $C=O$  functional group and a  $CH$  functional group. All carboxylic acids further comprise a  $C-OH$  moiety that comprises  $C-O$  and  $OH$  functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The  $CH$  functional group was solved in the Hydrogen Carbide ( $CH$ ) section except that the energy of the  $C-H$  MO is matched to the carbon-atom contribution to  $\Delta E_{H_2MO}(AO/HO)$  and  $E_T(atom-atom, msp^3.AO)$  of the  $C-O$  group. The alkyl carboxylic acid  $C=O$  and  $C-C(O)$  groups are equivalent to those given in the Aldehydes section except that  $\bar{E}_{Kvib}$  is that of a carboxylic acid. The formic acid  $C=O$  group is solved equivalently to that of the alkyl carboxylic acid group, except that  $\Delta E_{H_2MO}(AO/HO)$  and  $E_T(atom-atom, msp^3.AO)$  correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the  $C=O$  MO due to the presence of a  $H$  bound to the carbonyl carbon. Also,  $\bar{E}_{Kvib}$  is that corresponding to formic acid. The  $C-O$  and  $OH$  groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the  $C-O$  MO is matched to that of the  $C=O$  group and  $\bar{E}_{Kvib}$  is that of a carboxylic acid.  $\Delta E_{H_2MO}(AO/HO)$  of the  $C-O$  group is equal to  $E_T(atom-atom, msp^3.AO)$  of the alkyl  $C=O$  group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones,  $E_T(atom-atom, msp^3.AO)$  of the  $C=O$ -bond MO in Eq. (15.52) of alkyl carboxylic acids due to the charge donation from the  $C$  and  $O$



atoms to the MO is  $-2.69893 \text{ eV}$  which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the  $C$  atom and the pair of AO electrons of the carbonyl  $O$  atom. It is given as a linear combination of the energy contributions corresponding to a double bond,  $-1.13379 \text{ eV}$  (Eq. (14.247)), and a triple bond,  $-1.56513 \text{ eV}$  (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl  $C2sp^3$  HO electron with the  $O$  of the  $C-O$ -bond MO in addition to the pair involved directly in the double bond with the carbonyl  $O$ .

$E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the formic acid  $C=O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-3.58557 \text{ eV}$ . This is also an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the  $C$  atom and the pair of AO electrons of the carbonyl  $O$  atom. It is given as a linear combination of the energy contributions corresponding to a triple bond,  $-1.56513 \text{ eV}$  (Eq. (14.342)), and a quadruple bond,  $-2.02043 \text{ eV}$  (Eqs. (15.18-15.21) with  $s=4$ ) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a  $H$  bound to the carbonyl carbon.

$E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the carboxylic acid  $C-C(O)$  group is equivalent to that of alkanes and aldehydes,  $-1.85836 \text{ eV}$ , where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the carboxylic acid. As in the case of aldehydes,  $C_{1o} = 2C_1$  in Eq. (15.52).

$E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the carboxylic acid  $C-O$  group is equivalent to that of alkyl alcohols,  $-1.85836 \text{ eV}$ . It is based on the energy match between the  $O$  AO and the  $C2sp^3$  HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513).  $E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C-O$  group matches that of the  $C-C(O)$  group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each  $E_D(\text{group})$  of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired



electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table 15.104.

Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

Functional Group	Group Symbol
CH (formic acid) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formic acid)	$C=O$ (i)
C=O (alkyl carboxylic acid)	$C=O$ (ii)
(O)C-O	$C-O$
OH group	$OH$
CH <sub>3</sub> group	$C-H$ ( $CH_3$ )
CH <sub>2</sub> group	$C-H$ ( $CH_2$ )
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)



Table 15.100. The geometrical bond parameters of alkyl carboxylic acids and experimental values [1].

Parameter	C-H (i)	C-O (i)	C=O (i)	C=O (ii)	OH	C-H (CH <sub>2</sub> )	C-H (CH <sub>3</sub> )	C-H (i)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
<i>a</i> (Å)	1.61341	2.04740	1.20799	1.29907	1.26430	1.67122	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
<i>c'</i> (Å)	1.03711	1.43087	1.13613	1.13977	0.91803	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length (Å)	1.09763	1.20243	1.20628	1.20628	0.971651	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.097 (formic acid)	1.202 (formic acid)	1.214 (acetic acid)	1.393 (methyl formate)	0.972 (formic acid)	1.107 (C-H propane)	1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane)	1.531 (butane)	1.531 (propane)	1.532 (propane)	1.531 (butane)	1.532 (propane)
<i>b</i> (Å)	1.23591	1.46439	0.61267	0.62331	1.12915	0.86925	0.72615	0.63095	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
<i>c</i>	0.64281	0.69887	0.88018	0.87737	0.75921	0.65380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.101. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acids.  $E_r$ ,  $R$ ,  $R'$ ,  $R''$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{m.p.}, \Delta O)$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $E_{\text{Total}}$ (eV)	$r_{\text{final}}$ (Å)	$r_{\text{final}}$ (Å)	$E_{\text{Total}}$ (eV) Final	$\theta'$ (°)	$\theta_i$ (°)	$\theta_j$ (°)	$d_i$ (Å)	$d_j$ (Å)
$RC(O)O-H$	O	-0.92918	0	0	0	-154.33766	1.00000	0.86359	-15.75493	115.09	64.91	64.12	0.55182	0.56625
$HC(O)O-H$	O	-0.92918	0	0	0	-154.33766	1.00000	0.86359	-15.75493	101.32	78.68	48.58	1.14765	0.16950
$HC(O)O-H$	C	-0.92918	-1.79278	0	0	-154.33766	0.91771	0.77536	-17.54772	93.94	86.06	43.24	1.26386	0.63229
$HC(O)O-H$	O	-0.92918	0	0	0	-154.33766	1.00000	0.86359	-15.75493	101.32	78.68	48.58	1.14765	0.16950
$HC(O)O-H$	C	-0.92918	-1.34946	-0.92918	0	-154.33766	0.91771	0.75447	-17.84271	91.96	88.04	41.90	1.39138	0.62578
$HC(O)O-H$	O	-1.79278	0	0	0	-154.33766	1.00000	0.86359	-16.61853	131.10	42.90	65.45	0.56355	0.59978
$HC(O)O-H$	C	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.75336	-17.54772	133.24	44.76	63.02	0.38561	0.55053
$RC(O)O-H$	O	-1.34946	0	0	0	-154.33766	1.00000	0.86359	-16.17531	137.27	42.73	66.31	0.21193	0.61784
$RC(O)O-H$	C	-1.34946	-0.92918	-0.92918	0	-154.33766	0.91771	0.75447	-17.84271	133.47	46.53	61.46	0.20972	0.51905
$HC(O)O-H$	C	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	69.89	110.11	36.09	1.30373	0.26662
$HC(O)O-H$	C	-0.92918	-1.34946	-0.92918	0	-154.33766	0.91771	0.75447	-18.03358	56.25	123.75	25.37	1.85902	0.41915
$HC(O)O-H$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	72.37	107.73	34.17	1.03988	0.32001
$HC(O)O-H$	C	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	65.99	114.01	30.58	1.76270	0.33183
$HC(O)O-H$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	77.49	102.51	41.48	1.25584	0.18708
$HC(O)O-H$	C	-0.92918	0	0	0	-153.47405	0.91771	0.81549	-16.68412	68.47	111.55	35.84	1.35486	0.29933
$HC(O)O-H$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77536	-17.61330	61.10	118.90	31.37	1.42988	0.37226
$HC(O)O-H$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	63.82	116.18	30.08	1.83879	0.38106
$HC(O)O-H$	C	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68412	56.41	123.59	26.06	1.90890	0.45117
$HC(O)O-H$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77536	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$HC(O)O-H$	C	-0.92918	-0.72457	-0.72457	0	-154.71860	0.91771	0.75889	-17.92866	48.21	131.79	21.74	1.95734	0.50570
$HC(O)O-H$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77536	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$HC(O)O-H$	C	-0.92918	-0.72457	-0.72457	0	-154.71860	0.91771	0.76065	-17.92866	50.04	129.96	22.66	1.94462	0.49298
$HC(O)O-H$	C	-0.92918	-0.72457	-0.72457	0	-154.71860	0.91771	0.76155	-17.92866	52.78	127.22	21.04	1.93443	0.47279
$HC(O)O-H$	C	-0.92918	-0.72457	-0.72457	0	-154.71860	0.91771	0.76165	-17.92866	50.04	129.96	22.66	1.94462	0.49298



Table 15.102. The energy parameters (eV) of functional groups of alkyl carboxylic acids

Parameters	C-H (i)	C-C (O)	C=O (i)	C=O (ii)	OH	C-H <sub>2</sub>	C-H <sub>3</sub>	C-H (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
$\eta_1$	1	1	2	2	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	0	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\eta_4$	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\eta_5$	0.75	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\eta_6$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_7$	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1
$\eta_8$	0.91771	0.91771	0.85395	0.85395	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\eta_9$	0	0	2	2	0	0	1	1	0	0	0	1	1	0
$\eta_{10}$	1	2	4	4	1	1	1	1	2	2	2	2	2	2
$\eta_{11}$	1	0	0	0	0	3	2	1	0	0	0	0	0	0
$\eta_{12}$	0.75	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\eta_{13}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{14}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{15}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{16}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{17}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{18}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{19}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{20}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{21}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{22}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{23}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{24}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{25}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{26}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{27}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{28}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{29}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{30}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{31}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{32}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{33}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{34}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{35}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{36}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{37}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{38}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{39}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{40}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{41}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{42}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{43}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{44}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{45}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{46}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{47}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{48}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{49}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{50}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{51}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{52}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{53}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{54}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{55}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{56}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{57}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{58}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{59}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{60}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{61}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{62}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{63}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{64}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{65}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{66}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{67}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{68}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{69}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{70}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{71}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{72}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{73}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{74}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{75}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{76}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{77}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{78}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{79}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{80}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{81}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{82}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{83}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{84}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{85}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{86}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{87}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{88}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{89}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{90}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{91}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{92}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{93}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{94}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{95}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{96}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{97}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{98}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{99}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\eta_{100}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Table 15.103. The total bond energies of alkyl carboxylic acids calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{p(i=1-10)}$  values based on composition is given by (15.57).

Formula	C-H (i)	C-C (O)	C=O (i)	C=O (ii)	OH	C-H <sub>2</sub>	C-H <sub>3</sub>	C-H (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	$E_{mag}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
Formic acid	1	1	1	1	1	0	0	0	0	0	0	0	0	0	0	21.0945	21.036	0.00079
Acetic acid	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	33.5316	33.537	-0.00066
Propionic acid	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0	45.71686	45.727	-0.00022
Butyric acid	1	1	1	1	1	1	1	1	0	0	0	0	0	0	0	57.84156	57.883	-0.00015
Pentanoic acid	1	1	1	1	1	1	1	1	1	0	0	0	0	0	0	70.03236	69.995	-0.00035
Hexanoic acid	1	1	1	1	1	1	1	1	1	1	0	0	0	0	0	82.16482	82.183	-0.00011
2,2-Dimethylpropanoic acid	1	1	1	1	1	1	1	1	1	1	1	0	0	0	0	94.31679	93.689	-0.00068
Heptanoic acid	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	106.29726	106.247	-0.00049
Octanoic acid	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0	118.6306	118.666	-0.00032</



Table 15.104. The bond angle parameters of alkyl carboxylic acids and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{resp. } AO)$ .

Atom of Angle	$2\sigma_1$ ( $\sigma_1$ )	$2\sigma_2$ ( $\sigma_2$ )	$2\sigma_3$ ( $\sigma_3$ )	$F_{\text{Hybridization}}$ Atom 1 (Table 15.1 A)	$F_{\text{Hybridization}}$ Atom 2 (Table 15.1 A)	$c_1$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_3$	$c_4$	$E_T$ (eV)	$\theta_i$ ( $^\circ$ )	$\theta_j$ ( $^\circ$ )	$\theta_k$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$ZHC(O)_2$	2.06398	2.27227	3.9816	-15.55033 $C_s$	-15.55033 $C_s$	0.87495	0.85395 (Eq. (15.114))	0.75	1	0.75	0.97600	0				126.88	124.1 (formic acid)
$ZHC(O)_2$ (CH (O))	2.06398	2.63431	3.9816	-15.55033 $C_s$	-15.55033 $C_s$	0.87495	0.85395 (Eq. (15.114))	0.75	1	0.75	0.97600	0				110.76	
$ZOC(O)_2$	2.27227	2.63431	4.3243	-16.61853 $O_s$	-15.75493 $O_s$	0.81871	0.86359	1	1	1	0.84115	-1.44915				123.44	124.9 (formic acid)
$ZC(O)_2H$	2.63431	1.85616	3.6405	-14.82575 $H$	-14.82575 $H$	1	0.91771	0.75	1	0.75	0.91771	0				107.71	106.3 (formic acid)
$ZC(O)_2O$	2.8675	2.27954	4.3826	-16.0411 $O_s$	-13.61896 $O_s$	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.63376				125.70	126.6 (acetic acid)
$ZOC(O)_2$	2.8675	2.63431	4.914	-15.75493 $O_s$	-13.61896 $O_s$	0.86359	0.85395 (Eq. (15.114))	1	1	1	0.83877	-1.4915				109.65	110.8 (acetic acid)
$ZOC(O)_2$	2.27954	2.63431	4.3818	-16.17521 $O_s$	-15.75493 $O_s$	0.84115	0.86359	1	1	1	0.85237	-1.44915				126.03	
$ZHC(O)_2$	2.1106	2.1106	3.4252	-15.75493 $H$	-14.82575 $H$	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propionic)
$ZC(O)_2C$													69.51			110.49	112 (propionic)
$ZC(O)_2H$																110.49	113.8 (butanoic)
$ZC(O)_2C$	2.09711	2.09711	3.4252	-15.75493 $H$	-14.82575 $H$	0.86359	1	1	1	0.75	1.15796	0				109.50	110.8 (butanoic)
$ZC(O)_2H$													70.56			109.44	
$ZC(O)_2C$	2.91547	2.91547	4.7958	-16.0412 $C_s$	-16.0412 $C_s$	0.81549	0.81549	1	1	1	0.81549	-1.83856				110.67	110.8 (butanoic)
$ZC(O)_2H$	2.91547	2.11325	4.1633	-15.50033 $C_s$	-14.82575 $C_s$	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$ZC(O)_2H$	2.91547	2.69711	4.1633	-15.50033 $C_s$	-14.82575 $C_s$	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (butanoic)
$ZC(O)_2C$	2.90327	2.90327	4.7958	-15.50033 $C_s$	-14.82575 $C_s$	0.87495	0.91771	0.75	1	0.75	1.04887	-1.83856				111.27	111.4 (butanoic)
$ZC(O)_2C$													72.50			107.50	



CARBOXYLIC ACID ESTERS ( $C_nH_{2n}O_2$ ,  $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl carboxylic acid esters,  $C_nH_{2n}O_2$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. Formic acid ester has a  $HC=O$  moiety that comprises a more stable  $C=O$  functional group and a  $CH$  functional group. All carboxylic acid esters further comprise a  $COR$  moiety that comprises a  $C-O$  functional group and three types of  $O-R$  functional groups, one for  $R$  comprising methyl, one for  $R$  comprising an alkyl ester group of a formate, and one for  $R$  comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The  $CH$  functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester  $C=O$  and  $C-C(O)$  groups are equivalent to those given in the Carboxylic Acids section. The formic acid ester  $C=O$  group is equivalent to that given in the Carboxylic Acids section except that  $\bar{E}_{Kvib}$  is that corresponding to a formic acid ester. The  $C-O$  group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state,  $\bar{E}_D$  ( $eV$ ) and  $\bar{E}_{Kvib}$ , are those of a carboxylic acid ester. As in the case with the alkyl ethers, each  $O-C$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $O$  AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the  $O-C$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the  $O-C$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ .



$E_T(\text{atom} - \text{atom}, msp^3.AO)$  (Eq. (15.52)) of (1) the  $C = O$  group of alkyl carboxylic acid esters, (2) the  $C = O$  group of formic acid esters, (3) the alkyl carboxylic acid ester  $C - C(O)$  group, and (4) the carboxylic acid ester  $C - O$  group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are  
 5  $-2.69893 \text{ eV}$ ,  $-3.58557 \text{ eV}$ ,  $-1.85836 \text{ eV}$ , and  $-1.85836 \text{ eV}$ , respectively.  
 $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C - O$  group matches that of the  $C - C(O)$  group. Also, as in the case of aldehydes,  $C_{1o} = 2C_1$  in Eq. (15.52) for the  $C - C(O)$  group.

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $O - C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-1.13379 \text{ eV}$  for the  $O - CH_3$  group of  
 10 formate and alkyl carboxylates,  $-1.44915 \text{ eV}$  for the  $O - R$  group of alkyl carboxylates, and  $-1.85836 \text{ eV}$  for the  $O - R$  group of alkyl formates, where  $R$  is an alkyl group. Each is based on the energy match between the  $O$  AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), the  $C2sp^3$  HO of the methyl or alkyl ester group, and the carbonyl carbon. The increasing energy contributions to the single bond  
 15 correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are  $-1.13379 \text{ eV}$  (Eq. (14.247)), two times  $-0.72457 \text{ eV}$  (Eq. (14.151)), and two times  $-0.92918 \text{ eV}$  (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table  
 20 15.105. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.108 corresponding to functional-group composition of the  
 25 molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.79-15.108) are given in Table 15.110.



Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

Functional Group	Group Symbol
CH (formic acid ester) group	$C - H$ (i)
C-C(O)	$C - C(O)$
C=O (formic acid ester)	$C = O$ (i)
C=O (alkyl carboxylic acid ester)	$C = O$ (ii)
(O)C-O	$C - O$
O-CH <sub>3</sub>	$O - C$ (i)
O-R (formic acid ester)	$O - C$ (ii)
O-R (alkyl acid ester)	$O - C$ (iii)
OH group	$OH$
CH <sub>3</sub> group	$C - H$ (CH <sub>3</sub> )
CH <sub>2</sub> group	$C - H$ (CH <sub>2</sub> )
CH (alkyl) group	$C - H$ (ii)
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 15.106. The geometrical bond parameters of alkyl carboxylic acid esters and experimental values [1].

Parameter	C-H (i) Group	C-C(O) Group	C=O (i) Group	C=O (ii) Group	C-O Group	O-C (i) Group	O-C (ii) Group	O-C (iii) Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H (iii) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a$ (Å)	1.61341	2.04740	1.290799	1.29907	1.73490	1.82683	1.78255	1.80717	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.03711	1.43087	1.13613	1.13977	1.31716	1.35160	1.35112	1.34431	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.09763	1.51437	1.20243	1.20628	1.39402	1.43047	1.41303	1.42276	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.101 (methyl formate)	1.520 (acetic acid)	1.206 (methyl formate)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.08 (methyl formate) 1.107 (C-H propane) 1.117 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c$ (Å)	1.23591	1.46439	0.61267	0.62331	1.12915	1.22901	1.18107	1.20776	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.64281	0.69887	0.88078	0.87737	0.75921	0.73986	0.74900	0.74388	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.107. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid esters.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy C2sp <sup>2</sup> (eV)	$r_{\text{bond}}$ ( $a_0$ )	$r_{\text{bond}}$ ( $a_0$ )	$E_{\text{C2sp}^2}$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$RC_n(O)O-C_nH_{2n+1}$ (O-C (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183	90.63	89.37	42.70	1.34246	0.00914
$RC_n(O)O-C_nH_{2n+1}$ (O-C (ii))	C <sub>n</sub>	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	95.01	84.99	45.76	1.27445	0.07716
$HC_n(O)O-C_nH_{2n+1}R$ (O-C (iii))	O	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68412	93.09	86.91	43.59	1.29113	0.04939
$HC_n(O)O-C_nH_{2n+1}R$ (O-C (iii))	C <sub>n</sub>	-0.92918	-0.92918	0	0	-153.74005	0.91771	0.81549	-16.68411	93.09	86.91	43.59	1.29113	0.04939
$R'C_n(O)O-C_nH_{2n+1}R$ (O-C (iii))	O	-0.92918	-0.72457	0	0		1.00000	0.82562	-16.47951	91.72	88.28	43.10	1.31951	0.02480
$R'C_n(O)O-C_nH_{2n+1}R$ (O-C (iii))	C <sub>n</sub>	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	91.72	88.28	43.10	1.31951	0.02480
$HC_n(O)O-C_nH_{2n+1}$ (C=O (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183	98.97	81.03	46.82	1.18716	0.13300
$HC_n(O)O-C_nH_{2n+1}$ (C=O (ii))	C <sub>n</sub>	-0.56690	-1.79278	0	0	-154.33765	0.91771	0.77556	-17.54772	93.94	86.06	43.24	1.26386	0.05329
$HC_n(O)O-C_nH_{2n+1}$ (O-C (iii))	O	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68412	97.48	82.52	45.73	1.21100	0.10616
$HC_n(O)O-C_nH_{2n+1}$ (O-C (iii))	C <sub>n</sub>	-1.79278	-0.92918	0	0	-154.33765	0.91771	0.77556	-17.54772	93.94	86.06	43.24	1.26386	0.05329
$R'H_2C_2C_2(O)-OC_nH_{2n+1}$ (C=O (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183	98.97	81.03	46.82	1.18716	0.13300
$R'H_2C_2C_2(O)-OC_nH_{2n+1}$ (C=O (ii))	C <sub>n</sub>	-0.56690	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	91.96	88.04	41.90	1.29138	0.02578
$R'H_2C_2C_2(O)-OC_nH_{2n+1}R$ (C=O (iii))	O	-0.92918	-0.72457	0	0		1.00000	0.82562	-16.47951	98.32	81.68	46.34	1.19766	0.11949
$R'H_2C_2C_2(O)-OC_nH_{2n+1}R$ (C=O (iii))	C <sub>n</sub>	-0.72457	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	91.96	88.04	41.90	1.29138	0.02578
$HC_n(OR)=O$ (C=O (i))	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853	137.10	42.90	65.45	0.53635	0.59978
$HC_n(OR)=O$ (C=O (ii))	C <sub>n</sub>	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77556	-17.54772	135.24	44.76	63.02	0.38561	0.55053
$R'C_nH_2C_2(OR)=O$ (C=O (iii))	O	-1.34946	-0.92918	0	0		1.00000	0.84115	-16.17521	137.27	42.73	66.31	0.32193	0.61784
$R'C_nH_2C_2(OR)=O$ (C=O (iii))	C <sub>n</sub>	-1.34946	-0.92918	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	133.47	46.53	61.46	0.62072	0.51905
$H-C(O)OR$ (C-H (i))	C	-1.79278	-0.92918	0	0		0.91771	0.77556	-17.54772	69.89	110.11	36.09	1.30373	0.26662
$R'H_2C_2-C_2(O)OR$ (C-H (ii))	C <sub>n</sub>	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	56.25	123.75	25.37	1.85002	0.41915
$H_2C_2-C_2(O)OR$ (C-H (iii))	C <sub>n</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75495	72.27	107.75	34.17	1.63888	0.26501
$R'H_2C_2C_2-C_2(O)OR$ (C-H (iv))	C <sub>n</sub>	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	68.91	114.01	30.38	1.70270	0.33183
$C-H (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75495	77.49	102.51	41.48	1.23564	0.18708
$C-H (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	68.47	111.53	35.84	1.35486	0.29953



Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $C_{2sp^3}$ (eV)	$r_{final}$ ( $a_0$ )	$r_{final}$ ( $a_0$ )	$E_{calculated}$ (eV) Final	$E(C_{2sp^3})$ (eV) Final	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H$ (i)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	118.90	31.37	1.42988	0.37526
$H_1C_1C_2H_2$ (ii)	C <sub>1</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	116.18	30.08	1.83879	0.38106
$H_1C_1C_2H_2$ (iii)	C <sub>2</sub>	-0.92918	-0.92918	0	0	-153.47906	0.91771	0.81549	-16.68412	-16.49325	125.59	26.06	1.50890	0.45117
$R-H_1C_1C_2H_2$ (iv)	C <sub>1</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	131.70	21.90	1.97162	0.51388
$R-H_1C_1C_2H_2$ (v)	C <sub>2</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.73889	-17.92866	-17.73779	131.79	21.74	1.95734	0.50570
$rac-C_1C_2H_2$ (vi)	C <sub>1</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	131.70	21.90	1.97162	0.51388
$rac-C_1C_2H_2$ (vii)	C <sub>2</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	129.96	22.66	1.94462	0.49298
$rac-C_1C_2H_2$ (viii)	C <sub>1</sub>	-0.72457	-0.72457	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21785	127.22	24.04	1.92443	0.47279
$rac-C_1C_2H_2$ (ix)	C <sub>2</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.13599	0.91771	0.76765	-17.92866	-17.73779	129.96	22.66	1.94462	0.49298



Table 15.108. The energy parameters (eV) of functional groups of alkyl carboxylic acid esters.

Parameters	C-H (i)	C-C(O)	C=O (i)	C=O (ii)	C-O	O-C (i)	O-C (ii)	O-C (iii)	CH <sub>3</sub>	CH <sub>2</sub>	C-H (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
$n_1$	1	1	2	2	1	1	1	1	3	2	1	1	1	1	1	1	1
$n_2$	0	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.91771	0.91771	0.85395	0.85395	0.85395	0.85395	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	2	2	0	0	0	0	0	1	1	0	0	0	1	1	0
$C_6$	1	2	4	4	2	2	2	2	1	1	1	2	2	2	2	2	2
$C_7$	1	0	0	0	0	0	0	0	3	2	1	0	0	0	0	0	0
$C_{10}$	0.75	1	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{20}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$V_c$ (eV)	-36.74167	-30.19634	-112.61934	-111.25473	-35.08488	-32.67173	-33.78830	-33.15757	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p$ (eV)	13.11890	9.50874	23.95107	23.97467	10.32968	10.06642	10.19070	10.12103	38.97278	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T$ (eV)	11.38634	7.37432	43.62389	42.82081	10.11150	8.94219	9.47754	9.17389	32.55914	21.06675	10.48382	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m$ (eV)	-5.69317	-3.68716	-21.81195	-21.41040	-5.05575	-4.47110	-4.73877	-4.58695	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{\text{w}}^{\text{w}}(eV)$	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{\text{H},\text{H}}^{\text{H}}(eV)$	-0.92918	0	-3.58557	-2.69893	-2.69893	-1.13379	-1.85836	-1.44915	0	0	0	0	0	0	0	0	0
$E_{\text{r}}^{\text{r}}(eV)$	-13.70571	-14.63489	3.58557	2.69893	-11.93596	-13.50110	-12.77653	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{\text{r}}^{\text{r}}(eV)$	-31.63550	-31.63554	-63.27075	-63.27074	-31.63541	-31.63551	-31.63556	-31.63553	-67.69451	-49.66493	-31.63553	-31.63557	-31.63557	-31.63557	-31.63557	-31.63557	-31.63557
$E_{\text{r}}^{\text{r}}(eV)$	0	-1.85836	-3.58557	-2.69893	-1.85836	-1.13379	-1.85836	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{\text{r}}^{\text{r}}(eV)$	-31.63537	-33.49373	-66.85630	-65.96966	-33.49373	-32.76916	-33.49373	-33.08452	-67.69450	-49.66493	-31.63557	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^{15}$ rad/s)	26.0575	23.3291	60.9581	59.4034	12.7926	21.4555	22.7749	12.0329	74.9786	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	15.4846	15.4846
$E_{\text{r}}^{\text{r}}(eV)$	17.15150	15.35563	40.12366	39.10034	8.42030	14.12224	14.99085	7.92028	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	10.19220	10.19220
$E_{\text{r}}^{\text{r}}(eV)$	-0.25920	-0.25966	-0.41891	-0.40804	-0.19228	-0.24562	-0.25655	-0.18420	-0.25552	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.20896	-0.20896
$E_{\text{r}}^{\text{r}}(eV)$	0.35532	0.10502	0.21747	0.21077	0.14965	0.11469	0.11469	0.16118	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{\text{r}}^{\text{r}}(eV)$	(13.4581)	[29]	[32]	[12]	[32]	[32]	[32]	[4]	(Eq. (13.4581))	(Eq. (13.4581))	(Eq. (13.4581))	[2]	[4]	[5]	[2]	[2]	[2]
$E_{\text{r}}^{\text{r}}(eV)$	-0.08153	-0.20715	-0.31017	-0.30266	-0.11745	-0.18628	-0.19921	-0.10361	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{\text{r}}^{\text{r}}(eV)$	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\text{r}}^{\text{r}}(eV)$	-31.71690	-33.70088	-67.47664	-66.57498	-33.61118	-32.95544	-33.69294	-33.18813	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{\text{r}}^{\text{r}}(eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{r}}^{\text{r}}(eV)$	0	0	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\text{r}}^{\text{r}}(eV)$	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844
$E_{\text{r}}^{\text{r}}(eV)$	3.48357	4.43110	8.70826	7.80660	4.34141	3.68566	4.42316	3.91835	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.97398



Table 15.109. The total bond energies of alkyl carboxylic acid esters calculated using the functional group composition and the energies of Table 15.108 compared to the experimental values [3]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_{\text{group}}$  ( $\text{eV}$ ) values based on composition is given by (15.57).

[illegible]



Table 15.110. The bond angle parameters of alkyl carboxylic acid esters and experimental values [1]. In the calculation of  $\theta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{exp. AO})$ .

Atoms of angle	$2c^1$ Bond 1 ( $\theta_1$ )	$2c^2$ Bond 2 ( $\theta_2$ )	$2c^3$ Terminal Atoms ( $\theta_3$ )	$I_r^{\text{calculated}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$I_r^{\text{calculated}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c_2'$	$E_r$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle HC_1 O_1$ (C-H (i); C=O (i))	2.09711	2.70321	3.9463	-15.75493 $C_a$	7	-13.61806 $O_a$	O	0.86339	0.83395 (Eq. (15.11.4))	0.75	1	0.75	0.98884	0				109.95	110 (methyl formate)
$\angle O_1 C_1 O_1$ (C-H (i); C=O (i))	2.27227	2.63431	4.4043	-16.61853 $O_a$	23	-16.68412 $O_a$	25	0.81871	0.81549	1	1	1	0.81710	-1.65376				127.56	127 (methyl formate)
$\angle C_1 O_1 C_1$ (CH (i); C=O (i))	2.70321	2.63431	4.4833	-16.32183 $C_a$	16	-18.47690 $C_a$	50	0.83360	0.73637	1	1	1	0.78498	-1.85836				114.27	114 (methyl formate)
$\angle HC_1 H$ Methylene	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86339	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_1 C_1 C_1$															69.31			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_1 C_1 H$																			111.0 (butane) 111.4 (isobutane)
$\angle HC_1 H$ Methyl	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86339	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_1 C_1 C_1$															70.56			109.44	
$\angle C_1 C_1 H$															70.56			109.44	
$\angle C_1 C_1 C_1$ iso $C_a$	2.91547	2.91547	4.7958	-16.68412 $C_a$	25	-16.68412 $C_a$	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_1 C_1 H$ iso $C_a$	2.91547	2.11323	4.1633	-15.55033 $C_a$	5	-14.82575 $C_a$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_1 C_1 H$ iso $C_a$	2.91547	2.09711	4.1633	-15.55033 $C_a$	5	-14.82575 $C_a$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_1 C_1 C_1$ tert $C_a$	2.90327	2.90327	4.7958	-15.55033 $C_a$	5	-14.82575 $C_a$	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_1 C_1 C_1$															72.50			107.50	



# AMIDES ( $C_nH_{2n+1}NO$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl amides,  $C_nH_{2n+1}NO$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. Formamide has a  $HC=O$  moiety that comprises a more stable  $C=O$  functional group and a  $CH$  functional group that is equivalent to that of the  $CH$  (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso- $CH$  group of branched-chain-alkyl portion of the alkyl amide except that  $E_{mag}$  (Eq. (15.58)) is not subtracted from  $E_D(Group)$ . All amides further comprise a  $C-NH_2$  moiety that comprises a  $NH_2$  functional group and two types of  $C-N$  functional groups, one for formamide and the other for alkyl amides ( $RC(O)NH_2$  where  $R$  is alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The  $NH_2$  functional group was solved in the Dihydrogen Nitride ( $NH_2$ ) section except that the energy of the  $N-H$  MO is matched to the nitrogen-atom contribution to  $\Delta E_{H_2MO}(AO/HO)$  and  $E_r(atom-atom,msp^3.AO)$  of the  $C-N$  group. Both alkyl amide  $C=O$  groups and the  $C-C(O)$  group are equivalent to those given in the Carboxylic Acid Esters section except that  $\bar{E}_{Kvib}$  of the  $C-C(O)$  group is matched to that of an amide. The  $C-N$  groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the  $C-N$  MO is matched to that of the  $C=O$  group and  $\bar{E}_{Kvib}$  is that of an amide.  $\Delta E_{H_2MO}(AO/HO)$  of the  $C-N$  group is equal to  $E_r(atom-atom,msp^3.AO)$  of the alkyl  $C=O$  and  $C-N$  groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each  $C-N$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of



electrons between the  $C2sp^3$  HO and the  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the  $C-N$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-N$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ .

5  $E_T(atom - atom, msp^3.AO)$  (Eq. (15.52)) of the  $C=O$  group of alky amides and the  $C=O$  group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are  $-2.69893 \text{ eV}$  and  $-3.58557 \text{ eV}$ , respectively.

$E_T(atom - atom, msp^3.AO)$  of the amide  $C-C(O)$  group is the same as alkanes, 10 aldehydes, carboxylic acids, and carboxylic acid esters,  $-1.85836 \text{ eV}$ , where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes,  $C_{1o} = 2C_1$  in Eq. (15.52).

In order to match energy throughout the chain of the amide molecule,  $E_T(atom - atom, msp^3.AO)$  of the  $C-N$ -bond MO in Eq. (15.52) due to the charge donation 15 from the  $C$  and  $N$  atoms to the MO is  $-1.65376 \text{ eV}$ . It is based on the energy match between the  $C2sp^3$  HO of the carbonyl and the primary amino group  $NH_2$ . It is given by the linear combination of  $-0.92918 \text{ eV}$  (Eq. (14.513)) which matches the contiguous  $C-C(O)$  or  $HC(O)$  group and  $-0.72457 \text{ eV}$  (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

20 The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.114 corresponding 25 to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.116.



Table 15.111. The symbols of functional groups of alkyl amides.

Functional Group	Group Symbol
CH (formamide) group	$C - H$ (i)
C-C(O)	$C - C(O)$
C=O (formamide)	$C = O$ (i)
C=O (alkyl amide)	$C = O$ (ii)
(O)C-N (formamide)	$C - N$ (i)
(O)C-N (alkyl amide)	$C - N$ (ii)
NH <sub>2</sub> group	NH <sub>2</sub>
CH <sub>3</sub> group	$C - H$ (CH <sub>3</sub> )
CH <sub>2</sub> group	$C - H$ (CH <sub>2</sub> )
CH (alkyl) group	$C - H$ (ii)
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 15.112. The geometrical bond parameters of alkyl amides and experimental values [1].

Parameter	C-H (i) Group	C=O (i) Group	C=O (ii) Group	C-N (i) Group	C-N (ii) Group	NH <sub>2</sub> Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a$ (Å)	1.07465	2.04740	1.290799	1.70920	1.75370	1.32297	1.64920	1.67122	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.05661	1.43087	1.13613	1.30736	1.32427	0.97065	1.04856	1.05553	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.11827	1.51437	1.20243	1.38365	1.40155	1.02729	1.10974	1.11713	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.125 (formamide)	1.519 (acetamide) 1.520 (N-methylacetamide)	1.212 (formamide)	1.368 (formamide)	1.380 (acetamide)	1.027 (formamide) 1.022 (acetamide)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c$ (Å)	1.29924	1.46439	0.61267	1.10098	1.14968	0.89894	1.27295	1.29569	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.63095	0.69887	0.88018	0.76490	0.75513	0.73369	0.63380	0.63159	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.113. The MO to HO intercept geometrical bond parameters of alkyl amides.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{resp. } \Delta O)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy ( $\Delta O$ ) (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{calc}}^{\text{calc}}$ (eV) Final	$E_{\text{calc}}^{\text{calc}}$ (eV) Final	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$RC(O)N(H)-H$ ( $C=O$ (i) and (ii))	N	-0.82688	0	0	0	-15.63263	0.93084	0.86923	-15.63263	-15.63263	66.10	62.13	0.61843	0.33222
$HC(O)-NH_2$ ( $C=O$ (i))	N	-0.82688	0	0	0	-15.63263	0.93084	0.86923	-15.63263	-15.63263	76.07	50.02	1.09814	0.20922
$HC(O)-NH_2$ ( $C-N$ (i))	C	-0.82688	-1.79278	0	0	-15.23535	0.91771	0.77991	-17.44541	-17.25455	83.19	44.70	1.21492	0.09244
$RH_2C_2(O)-NH_2$ ( $C=O$ (i))	N	-0.82688	0	0	0	-15.63263	0.93084	0.86923	-15.63263	-15.63263	79.86	48.10	1.17127	0.15300
$RH_2C_2(O)-NH_2$ ( $C-N$ (i))	C	-0.82688	-1.34946	-0.92918	0	-15.472121	0.91771	0.75878	-17.93127	-17.74041	89.49	41.30	1.31755	0.00672
$HC_2(NH_2)=O$ ( $C=O$ (i))	O	-1.79278	0	0	0	-15.23535	1.00000	0.81871	-16.61853	-16.61853	42.90	65.45	0.53635	0.59978
$HC_2(NH_2)=O$ ( $C=O$ (ii))	C	-1.79278	-0.82688	0	0	-15.472121	0.91771	0.77991	-17.44541	-17.25455	44.56	63.28	0.58044	0.55569
$RC_2H_2(NH_2)=O$ ( $C=O$ (i))	O	-1.34946	0	0	0	-15.23535	1.00000	0.84115	-16.17521	-16.17521	42.73	66.31	0.52193	0.61784
$RC_2H_2(NH_2)=O$ ( $C=O$ (ii))	C	-1.34946	-0.82688	-0.92918	0	-15.472121	0.91771	0.75878	-17.93127	-17.74041	46.33	61.70	0.61582	0.52395
$H-C(O)NH_2$ ( $CH$ (i))	C	-1.79278	-0.82688	0	0	-15.472121	0.91771	0.77991	-17.44541	-17.25455	117.61	32.13	1.41810	0.36148
$RH_2C_2-C_2(O)NH_2$ ( $C_2$ )	C	-0.92918	-1.34946	-0.82688	0	-15.472121	0.91771	0.75878	-17.93127	-17.74041	122.98	25.76	1.84386	0.47299
$H_2C_2-C_2(O)NH_2$ ( $C_2$ )	C	-0.92918	0	0	0	-15.254487	0.91771	0.86359	-15.75493	-15.56407	107.73	34.17	1.69388	0.26301
$RH_2C_2H_2C_2-C_2(O)NH_2$ ( $C-C$ (i))	C	-0.92918	-0.92918	0	0	-15.347405	0.91771	0.81549	-16.68411	-16.49325	114.01	30.58	1.76270	0.33183
$C-C(H)(CH_2)$ ( $C-C$ (ii))	C	-0.92918	0	0	0	-15.254487	0.91771	0.86359	-15.75493	-15.56407	102.51	41.48	1.23564	0.18708
$C-C(H)(CH_2)$ ( $C-C$ (iii))	C	-0.92918	-0.92918	0	0	-15.347406	0.91771	0.81549	-16.68412	-16.49325	111.53	35.84	1.33486	0.29933
$H_2C_2-C_2H_2CH_2$ ( $C-C$ (i))	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.91771	0.77247	-17.61330	-17.42244	118.90	31.37	1.42988	0.37336
$H_2C_2-C_2H_2CH_2$ ( $C-C$ (ii))	C	-0.92918	0	0	0	-15.254487	0.91771	0.86359	-15.75493	-15.56407	116.18	30.08	1.83879	0.38106
$R-H_2C_2(H_2C_2-R)HCH_2$ ( $C-C$ (i))	C	-0.92918	-0.92918	0	0	-15.347406	0.91771	0.81549	-16.68412	-16.49325	123.59	26.06	1.50890	0.45117
$R-H_2C_2(H_2C_2-R)HCH_2$ ( $C-C$ (ii))	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.91771	0.77247	-17.61330	-17.42244	131.70	21.90	1.97162	0.51388
$R-H_2C_2(H_2C_2-R)HCH_2$ ( $C-C$ (iii))	C	-0.92918	-0.72457	-0.72457	-0.72457	-15.411860	0.91771	0.75889	-17.92866	-17.73779	131.79	21.74	1.95734	0.50570
$isoC_2C_2(H_2C_2-R)HCH_2$ ( $C-C$ (i))	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.91771	0.77247	-17.61330	-17.42244	131.70	21.90	1.97162	0.51388
$isoC_2C_2(H_2C_2-R)HCH_2$ ( $C-C$ (ii))	C	-0.72457	-0.72457	-0.72457	-0.72457	-15.411860	0.91771	0.75889	-17.92866	-17.73779	129.96	22.66	1.94462	0.49298
$isoC_2C_2(H_2C_2-R)HCH_2$ ( $C-C$ (iii))	C	-0.72457	-0.92918	-0.92918	0	-15.411860	0.91771	0.78155	-17.40869	-17.21783	127.22	24.04	1.92443	0.47279
$isoC_2C_2(H_2C_2-R)HCH_2$ ( $C-C$ (iv))	C	-0.72457	-0.72457	-0.72457	-0.72457	-15.411860	0.91771	0.76765	-17.92866	-17.73779	129.96	22.66	1.94462	0.49298



Table 15.114. The energy parameters (eV) of functional groups of alkyl amides.

Parameters	C-H (i)	C-C(O)	C=O (i)	C-N (i)	NH <sub>2</sub>	CH <sub>2</sub>	CH <sub>3</sub>	C-H (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	C-C (g)
$\eta_1$	1	1	2	1	2	3	3	1	1	1	1	1	1	1	1
$\eta_2$	0	0	0	0	0	2	2	0	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
$\zeta_1$	0.75	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_2$	1	1	1	1	0.93613	1	1	1	1	1	1	1	1	1	1
$\zeta_3$	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1	1
$\zeta_4$	0.91771	0.91771	0.85395	0.91140	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\zeta_5$	0	0	2	0	0	0	0	1	0	0	0	1	0	1	0
$\zeta_6$	1	2	4	2	1	1	1	1	2	2	2	2	2	2	2
$\zeta_7$	1	0	0	0	2	3	2	1	0	0	0	0	0	0	0
$\zeta_8$	0.75	1	0.5	0.5	1.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_9$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\zeta_{10}$	-35.12015	-30.19634	-112.61934	-38.24008	-78.77719	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
$\zeta_{11}$	12.87680	9.50874	23.95107	10.40705	28.03446	38.92728	25.78002	12.87680	9.53552	9.53552	9.53552	9.53552	9.53552	9.53552	9.53552
$\zeta_{12}$	10.48382	7.37432	43.62389	11.18655	29.77286	32.53914	21.06675	10.48382	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
$\zeta_{13}$	-5.24291	-3.68716	-21.81195	-5.59327	-14.88643	-16.26957	-10.33337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
$\zeta_{14}$	-14.63489	-14.63489	0	-14.63489	-14.53414	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,10}$ (eV)	0	0	-3.58557	-2.69893	-1.65376	0	0	0	0	0	0	0	0	0	0
$\Delta E_{1,10}$ (eV)	-14.63489	-14.63489	3.58557	2.69893	-12.88038	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,10}$ (eV)	0	0	0	0	-14.53414	0	0	0	0	0	0	0	0	0	0
$\Delta E_{1,10}$ (eV)	-31.63553	-31.63553	-63.27075	-31.63553	-49.66493	-67.69451	-49.66493	-31.63553	-31.63553	-31.63553	-31.63553	-31.63553	-31.63553	-31.63553	-31.63553
$\Delta E_{1,10}$ (eV)	0	-1.83836	-5.58557	-2.69893	-1.65376	0	0	0	-1.83836	-1.83836	-1.44915	-1.83836	-1.44915	-1.83836	-1.44915
$\Delta E_{1,10}$ (eV)	-31.63557	-33.49373	-66.85630	-65.90606	-33.28912	-48.73660	-67.69450	-31.63557	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\omega$ (10 <sup>15</sup> rad/s)	24.1759	14.1117	60.9581	59.4034	13.0822	12.5874	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	15.4846	9.43699	15.4846
$\bar{\nu}_{C-H}$ (eV)	15.91299	9.28860	40.12366	39.10034	8.61093	8.28256	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	10.19220	6.21159	10.19220
$\bar{\nu}_{C-H}$ (eV)	0.24966	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.20896	-0.16515	-0.20896
$\bar{\nu}_{C-H}$ (eV)	0.35532	0.14655	0.21747	0.17358	0.17358	0.17358	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.09944	0.12312	0.12312
$\bar{\nu}_{C-H}$ (eV)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)	(13.4588)
$\bar{\nu}_{C-H}$ (eV)	-0.07200	-0.12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.22757	-0.14502	-0.07200	-0.07200	-0.15924	-0.07200	-0.15924	-0.07200	-0.15924
$\bar{\nu}_{C-H}$ (eV)	0.14803	0.14803	0.14441	0.14441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$\bar{\nu}_{C-H}$ (eV)	-31.70737	-33.62241	-67.47664	-66.57498	-33.39559	-33.39559	-67.92207	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$\bar{\nu}_{C-H}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$\bar{\nu}_{C-H}$ (eV)	-13.59844	0	0	0	0	0	-13.59844	-13.59844	0	0	0	0	0	0	0
$\bar{\nu}_{C-H}$ (eV)	3.47404	4.52653	8.70826	7.80660	4.12581	4.12581	12.49186	7.80616	4.32754	4.29921	3.97598	4.17951	3.97598	4.17951	3.97598
$\bar{\nu}_{C-H}$ (eV)															

Table 15.115. The total bond energies of alkyl amides calculated using the functional group composition and the energies of Table 15.114 compared to the experimental values [3].

Formula	Name	C-H (i)	C-C(O)	C=O (i)	C-N (i)	NH <sub>2</sub>	CH <sub>2</sub>	CH <sub>3</sub>	C-H (ii)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> NO	Formamide	1	0	1	0	1	0	0	0	0	0	0	0	0	0	22.69712	22.697	0.00041
CH <sub>3</sub> NO	Acetamide	0	1	0	1	1	0	1	0	0	0	0	0	0	0	36.13222	36.103	-0.00015
CH <sub>3</sub> NO	Propanamide	0	1	0	1	1	1	1	0	0	0	0	0	0	0	48.30992	48.264	-0.00004
CH <sub>3</sub> NO	Butanamide	0	1	0	1	1	2	0	0	0	0	0	0	0	0	60.47762	60.449	-0.00003
CH <sub>3</sub> NO	2-Methylpropanamide	0	1	0	1	1	1	2	0	0	0	0	0	0	0	60.51559	60.435	-0.00009
CH <sub>3</sub> NO	Pentanamide	0	1	0	1	1	3	0	0	0	0	0	0	0	0	72.63232	72.441	-0.00209
CH <sub>3</sub> NO	2,2-Dimethylpropanamide	0	1	0	1	1	3	0	0	0	0	0	0	0	0	72.63232	72.441	-0.00209
CH <sub>3</sub> NO	Hexanamide	0	1	0	1	1	4	0	0	0	0	0	0	0	0	84.76302	84.760	-0.00004
CH <sub>3</sub> NO	Octanamide	0	1	0	1	1	6	0	0	0	0	0	0	0	0	109.09842	109.071	-0.00025



Table 15.116. The bond angle parameters of alkyl amides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{exp}, \text{AO})$ .

Atoms of Angle	$2c^1$ Bond 1 ( $a_1$ )	$2c^2$ Bond 2 ( $a_2$ )	$2c^3$ Terminal Atom ( $a_3$ )	$V_{\text{residual}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{residual}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$\zeta_2$ Atom 1	$\zeta_1$ Atom 2	$C_1$	$C_2$	$\zeta_1$	$\zeta_2$	$E_T$ (eV)	$\theta_i$ ( $^\circ$ )	$\theta_j$ ( $^\circ$ )	$\theta_k$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle \text{HNH}$	1.94130	1.94130	3.1464	-14.33414 $N$	N	H	H	0.93613 (Eq. (15.62))	1	1	1	0.75	1.06823	0				108.27	
$\angle \text{C}^{\text{H}} \text{NH}$ ( $\text{C}^{\text{H}}$ (i); $\text{C}_n = \text{O}$ (i))	2.61473	1.94130	3.9328	-14.33414 $N$	N	$\text{C}_n$	1	0.93613 (Eq. (15.62))	0.91771	0.75	1	0.75	0.98053	0				118.61	119.2 (formamide)
$\angle \text{HC}^{\text{H}} \text{N}$ ( $\text{CH}$ (i); $\text{C}_n = \text{O}$ (i))	2.11323	2.61473	4.0825	-14.82575 $\text{C}_n$	1	$N$	N	0.91771	0.93613 (Eq. (15.62))	0.75	1	0.75	1.02006	0				119.04	
$\angle \text{HC}^{\text{H}} \text{O}$ ( $\text{CH}$ (i))	2.11323	2.27227	3.7238	-14.82575 $\text{C}_n$	1	$\text{O}$	O	0.91771	0.83395 (Eq. (15.114))	0.75	1	0.75	0.93052	0				116.18	
$\angle \text{OC}^{\text{H}} \text{N}$ ( $\text{C}_n = \text{O}$ (i))	2.27227	2.61473	4.3359	16.17521 $\text{O}$	12	$N$	17	0.84115	0.83078	1	1	1	0.83596	-1.44915				124.91	125.0 (formamide)
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{N}$ ( $\text{C}_n = \text{O}$ (iii))	2.86175	2.64855	4.6904	-15.75493 $\text{C}_n$	7	$N$	N	0.86359	0.91140 (Eq. (15.116))	1	1	1	0.8749	-1.44915				116.63	115.1 (acetamide)
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{O}$ ( $\text{C}_n = \text{O}$ (iii))	2.86175	2.27954	4.5007	-16.68411 $\text{O}$	24	$\text{O}$	O	0.81549	0.83595 (Eq. (15.114))	1	1	1	0.83472	-1.63376				124.63	
$\angle \text{OC}^{\text{H}} \text{N}$ ( $\text{C}_n = \text{O}$ (iii))	2.27954	2.64855	4.3126	16.17521 $\text{O}$	12	$N$	17	0.84115	0.83078	1	1	1	0.83596	-1.44915				121.95	122.0 (acetamide)
$\angle \text{HC}^{\text{H}} \text{H}$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$															69.51			110.49	113.8 (butane) 110.8 (acetone) 111.0 (butane) 111.4 (acetone)
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{H}$															69.51			110.49	108.5 (acetone)
$\angle \text{HC}^{\text{H}} \text{H}$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.44	109.44
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$															70.56			109.44	
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{H}$															70.56			109.44	
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$ $\text{iso } \text{C}_n$	2.91547	2.91547	4.7958	-16.68412 $\text{C}_n$	25	$\text{C}_n$	25	0.81549	0.81549	1	1	1	0.81549	-1.85856				110.67	110.8 (isobutane)
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{H}$ $\text{iso } \text{C}_n$	2.91547	2.11323	4.1633	-15.35033 $\text{C}_n$	5	$\text{C}_n$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{H}$ $\text{iso } \text{C}_n$	2.91547	2.09711	4.1633	-15.55033 $\text{C}_n$	5	$\text{C}_n$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$ $\text{iso } \text{C}_n$	2.90327	2.90327	4.7958	-15.55033 $\text{C}_n$	5	$\text{C}_n$	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85856				111.27	111.4 (isobutane)
$\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$															72.50			107.50	



# N-ALKYL AND N,N-DIALKYL-AMIDES ( $C_nH_{2n+1}NO$ , $n = 2, 3, 4, 5 \dots \infty$ )

The N-alkyl and N,N-dialkyl amides,  $C_nH_{2n+1}NO$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. Formamide has a  $HC=O$  moiety that comprises a more stable  $C=O$  functional group and a  
 5  $CH$  functional group that is equivalent to that of the iso- $CH$  group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a  $C-N(R_1)R_2$  moiety that comprises two types of  $C-N$  functional groups, one for formamide and the other for alkyl amides ( $RC(O)N(R_1)R_2$  where  $R$  is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a  
 10 single methyl or alkyl substitution, the  $NH-C$  bond and  $NH$  are functional groups, and the  $N-C$  bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds.  
 15 The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or  
 20 N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The  $NH$  functional group was solved in the Hydrogen Nitride ( $NH$ ) section except that the energy of the  $N-H$  MO is matched to the nitrogen-atom contribution to  $\Delta E_{H_2MO}(AO/HO)$  and  $E_r(atom-atom, msp^3.AO)$  of the  $C-N$  group. The  $C-C(O)$  group, both N-alkyl or N,N-dialkyl amide  $C=O$  groups, and both  $C-N$  groups are equivalent to those given in the  
 25 Amides section.

As in the case of primary amines, each  $N-C$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the



$N-C$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.52) for the  $N-C$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ .

$E_r(atom - atom, msp^3.AO)$  of the N-substituted amide  $C-C(O)$  group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides,  $-1.85836 \text{ eV}$ , where  
 5 both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes,  $C_{1o} = 2C_1$  in Eq. (15.52).

$E_r(atom - atom, msp^3.AO)$  (Eq. (15.52)) of the  $C=O$  group of N-substituted alky amides and the  $C=O$  group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the  
 10 Carboxylic Acids section are  $-2.69893 \text{ eV}$  and  $-3.58557 \text{ eV}$ , respectively.

$E_r(atom - atom, msp^3.AO)$  of both  $C-N$  functional groups are the same as those of the corresponding groups of amides,  $-1.65376 \text{ eV}$ .  $E_r(atom - atom, msp^3.AO)$  of the singly-substituted  $NH-C$ -bond MO in Eq. (15.52) due to the charge donation from the  $N$  and  $C$  atoms to the MO is  $-0.92918 \text{ eV}$ . It is equivalent to that of tertiary amines and matches the  
 15 energy of the  $NH-C$  group to that of the  $C-N$  group wherein  $E_r(atom - atom, msp^3.AO)$  of the latter is a linear combination of  $-0.92918 \text{ eV}$  (Eq. (14.513)) and  $-0.72457 \text{ eV}$  (Eq. (14.151)).  $E_r(atom - atom, msp^3.AO)$  of the doubly-substituted  $N-C$ -bond MO is  $-0.72457 \text{ eV}$ . It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the  $N-C$  group to that of the  $C-N$  group by matching one of the  
 20 components of  $E_r(atom - atom, msp^3.AO)$  of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl  
 25 or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each  $E_p(group)$  of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122.



Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

Functional Group	Group Symbol
C-C(O)	$C - C(O)$
C=O (N-alkyl and N,N-dialkyl formamide)	$C = O$ (i)
C=O (N-alkyl and N,N-dialkyl amide)	$C = O$ (ii)
(O)C-N (N-alkyl and N,N-dialkyl formamide)	$C - N$ (i)
(O)C-N (N-alkyl and N,N-dialkyl amide)	$C - N$ (ii)
NH group	$NH$
N-C (N-alkyl)	$N - C$ (i)
N-C (N,N,-dialkyl)	$N - C$ (ii)
CH <sub>3</sub> group	$C - H$ (CH <sub>3</sub> )
CH <sub>2</sub> group	$C - H$ (CH <sub>2</sub> )
CH (alkyl) group	$C - H$
CC bond (n-C)	$C - C$ (a)
CC bond (iso-C)	$C - C$ (b)
CC bond (tert-C)	$C - C$ (c)
CC (iso to iso-C)	$C - C$ (d)
CC (t to t-C)	$C - C$ (e)
CC (t to iso-C)	$C - C$ (f)



Table 15.118. The geometrical bond parameters of N-alkyl and N,N-dialkyl amides and experimental values [1]

Parameter	C-C (f)	C-C (g)	C-C (h)	C-C (i)	C-C (j)	C-C (k)	C-C (l)	C-C (m)	C-H (CH <sub>3</sub> )	C-H (CH <sub>2</sub> )	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
$a$ (Å)	2.04740	1.200799	1.29907	1.70920	1.75370	1.28620	1.96313	1.97794	1.64920	1.67122	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$b$ (Å)	1.43087	1.13613	1.13977	1.30726	1.32427	0.95706	1.40112	1.40639	1.04856	1.05533	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length	1.51437	1.20243	1.20628	1.38365	1.40155	1.01291	1.48288	1.48846	1.10974	1.11713	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
$2c$ (Å)																
Exp. Bond Length	1.520 (N-methylacetamide)	1.212 (formamide)	1.225 (N-methylacetamide)	1.368 (formamide)	1.380 (acetamide)		1.469 (N-methylacetamide)		1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.531 (butane)	1.532 (propane)	1.531 (butane)	1.532 (propane)
$h, c$ (Å)	1.46439	0.61267	0.62331	1.10098	1.14968	0.85927	1.37505	1.39079	1.27295	1.29569	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$\sigma$	0.69887	0.88018	0.87737	0.76490	0.75513	0.74410	0.71372	0.71104	0.63580	0.63159	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.119. The MO to HO intercept geometrical bond parameters of N-alkyl and N,N-dialkyl amides.  $R, R', R''$  are H, methyl, or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{moy}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy (eV)	$r_{\text{bond}}$ ( $a_0$ )	$r_{\text{atom}}$ ( $a_0$ )	$E(\text{C}2\text{sp}^2)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$R'C_2(O)N(C_2H_5)-H$ (C=O (i) and (ii)) (C-N (i) and (ii))	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722	115.47	64.53	62.49	0.59403	0.36303
$R'C_2(O)N(H)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722	78.61	101.39	37.00	1.50779	0.16667
$R'C_2(O)N(H)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	C <sub>s</sub>	-0.46459	0	0	0	-151.08028	0.91771	0.88983	-15.26034	83.37	96.63	40.00	1.50383	0.10271
$R'C_2(O)N(H)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722	78.61	101.39	37.00	1.50779	0.16667
$R'C_2(O)N(H)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	C <sub>s</sub>	-0.46459	-0.92918	0	0	-151.00946	0.91771	0.83885	-16.21952	78.02	101.39	36.64	1.57525	0.17413
$R'C_2(O)N(C_2H_5)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720	75.57	104.43	35.35	1.61336	0.20697
$R'C_2(O)N(C_2H_5)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	C <sub>s</sub>	-0.36229	0	0	0	-151.07798	0.91771	0.89582	-15.18804	82.59	97.41	39.70	1.52188	0.11549
$R'C_2(O)N(C_2H_5C_2H_4R)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720	75.57	104.43	35.35	1.61336	0.20697
$R'C_2(O)N(C_2H_5C_2H_4R)-C_2H_5$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	C <sub>s</sub>	-0.36229	0	0	0	-151.07798	0.91771	0.89582	-15.18804	82.59	97.41	39.70	1.52188	0.11549
$R'C_2(O)N(R')-C_2H_5C_2H_4R$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720	75.57	104.43	35.35	1.61336	0.20697
$R'C_2(O)N(R')-C_2H_5C_2H_4R$ (C=O (i) and (ii)) (C-N (i) and (ii)) (N-C (i))	C <sub>s</sub>	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	77.12	102.88	36.28	1.59451	0.18812
$HC_2(O)-N(H)R$ (C=O (i)) (C-N (i)) (N-C (i)) <i>R = methyl or alkyl</i>	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722	102.07	77.93	48.57	1.13090	0.17647
$HC_2(O)-N(H)R$ (C=O (i)) (C-N (i)) (N-C (i)) <i>R = methyl or alkyl</i>	C <sub>s</sub>	-0.82688	-1.79278	0	0	-154.23535	0.91771	0.77991	-17.44541	96.81	83.19	44.70	1.21492	0.09244
$HC_2(O)-N(R)R$ (C=O (i)) (C-N (i)) (N-C (i)) <i>R, R' = methyl or alkyl</i>	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720	101.03	78.97	47.79	1.14842	0.15895
$HC_2(O)-N(R)R$ (C=O (i)) (C-N (i)) (N-C (i))	C <sub>s</sub>	-0.82688	-1.79278	0	0	-154.23535	0.91771	0.77991	-17.44541	96.81	83.19	44.70	1.21492	0.09244



$R, R' = \text{methyl or alkyl}$ $R^1H_2C_2C_2(O)-N(H)R$ (C=O (6)) (C-N (6)) (N-C (6)) $R = \text{methyl or alkyl}$	N	-0.82688	-0.4459	0	0	0	0.5084	0.8418	-16.1722	98.16	81.84	46.02	1.2046	0.1192
$R^1H_2C_2C_2(O)-N(H)R$ (C=O (6)) (C-N (6)) (N-C (6)) $R = \text{methyl or alkyl}$	C <sub>s</sub>	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	90.51	89.49	41.30	1.3155	0.00672
$R^1H_2C_2C_2(O)-N(R)R$ (C=O (6)) (C-N (6)) (N-C (6)) $R, R' = \text{methyl or alkyl}$	N	-0.82688	-0.36229	-0.36229	0		0.5084	0.8078	-16.37720	97.06	82.94	45.82	1.2220	0.10207
$R^1H_2C_2C_2(O)-N(R)R$ (C=O (6)) (C-N (6)) (N-C (6)) $R, R' = \text{methyl or alkyl}$	C <sub>s</sub>	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	90.51	89.49	41.30	1.3155	0.00672
$HC_4(N(R)R) = O$ (C=O (6)) $R, R' = H, \text{methyl, or alkyl}$	O	-1.70278	0	0	0		1.00000	0.81871	-16.61853	137.10	42.90	65.45	0.51655	0.59778
$HC_4(N(R)R) = O$ (C=O (6)) $R, R' = H, \text{methyl, or alkyl}$	C <sub>s</sub>	-1.70278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	135.44	44.56	63.28	0.58044	0.55569
$HC_4H_2C_2(N(R)R) = O$ (C=O (6)) $R, R' = H, \text{methyl, or alkyl}$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521	137.27	42.73	66.31	0.52193	0.61784
$HC_4H_2C_2(N(R)R) = O$ (C=O (6)) $R, R' = H, \text{methyl, or alkyl}$	C <sub>s</sub>	-1.34946	-0.82688	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	133.67	46.33	61.70	0.61582	0.52595
$H-C(O)N(R)R$ $R, R' = H, \text{methyl, or alkyl}$	C'	-1.70278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	62.39	117.61	32.13	1.41810	0.56148
$RH_2C_2-C_2(O)N(R)R$ $R, R' = H, \text{methyl, or alkyl}$	C <sub>s</sub>	-0.92918	-1.34946	-0.92688	0	-154.72121	0.91771	0.75878	-17.93127	57.02	122.98	25.76	1.84586	0.41599
$H_2C_2-C_2(O)N(R)R$ $R, R' = H, \text{methyl, or alkyl}$	C <sub>s</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	72.27	107.73	34.17	1.69388	0.36301
$RH_2C_2H_2C_2-C_2(O)N(R)R$ $R, R' = H, \text{methyl, or alkyl}$	C <sub>s</sub>	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	65.99	114.01	30.58	1.76270	0.33183
$C-H(CH_3)$ $C' = H(CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	77.49	102.51	41.48	1.2564	0.18708
$C-H(CH_3)$ $C' = H(CH_3)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	68.47	111.53	35.84	1.35486	0.29933
$H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	0	0	0	-154.40324	0.91771	0.77247	-17.61330	61.10	118.90	31.37	1.42988	0.37326
$H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	-0.92918	0	0	-152.54487	0.91771	0.86359	-15.75493	63.82	116.18	30.08	1.83879	0.38106
$R-H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75869	-17.93666	48.21	131.79	21.74	1.95734	0.50570
$R-H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75869	-17.93666	50.04	129.96	22.66	1.94462	0.49298
$R-H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	-0.72457	-0.92918	0	-154.19863	0.91771	0.76155	-17.48609	52.78	127.22	24.04	1.92443	0.47279
$R-H_2C_2H_2CH_2-$ $(C-C(6))$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.13199	0.91771	0.76155	-17.48609	50.04	129.96	22.66	1.94462	0.49298



Table 15.120. The energy parameters (eV) of functional groups of N-alkyl and N,N-dialkyl amides.

Parameters	C-C (V) Group	C=O (f) Group	C-N (f) Group	NH Group	N-C (f) Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\mu_1$	1	2	1	1	1	3	2	1	1	1	1	1	1	1
$\mu_2$	0	0	0	0	0	2	1	0	0	0	0	0	0	0
$\mu_3$	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.91771	0.85395	0.91140	1	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	2	0	0	0	0	0	1	0	0	0	1	1	0
$C_6$	2	4	2	2	2	1	1	1	2	2	2	2	2	2
$C_7$	0	0	0	0	0	3	2	1	0	0	0	0	0	0
$C_8$	1	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{20}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$I_1$ (eV)	-30.19634	-112.61934	-111.25473	-36.88558	-31.67393	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-29.10112	-29.10112	-29.10112
$I_2$ (eV)	9.50874	23.95107	23.87467	10.47075	9.70679	38.92728	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
$I_3$ (eV)	7.3432	43.62389	42.82081	11.18655	10.51650	15.90663	32.53914	21.06675	6.77464	6.77464	6.90500	6.74664	6.90500	6.90500
$I_4$ (eV)	-3.68716	-21.81195	-21.41040	-5.59327	-5.5825	-7.9482	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{1,100}^{\text{calc}}(\text{eV})$	-14.63489	0	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,100}^{\text{calc}}(\text{eV})$	0	-3.88257	-2.69893	-3.5268	-0.92918	-0.72457	0	0	0	0	0	0	0	0
$E_{2,100}^{\text{calc}}(\text{eV})$	-14.63489	3.8857	2.69893	-10.28221	-13.70571	-13.91032	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$I_5$ (eV)	-31.65334	-63.27075	-63.27074	-31.65337	-31.65337	-67.69451	-49.66493	-31.65337	-31.65337	-31.65337	-31.65337	-31.65337	-31.65337	-31.65337
$I_6$ (eV)	-1.85836	-3.8857	-2.69893	-1.65376	-0.92918	-0.72457	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$I_7$ (eV)	-33.49373	-66.85630	-65.96966	-33.28912	-32.55994	-67.69450	-49.66493	-31.65337	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\omega$ (10 <sup>3</sup> rad s <sup>-1</sup> )	14.1117	60.9581	59.4034	13.0822	12.5874	44.9494	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_8$ (eV)	9.28860	40.12566	39.10034	8.28526	6.9543	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{\nu}_{\text{C-H}}$ (cm <sup>-1</sup> )	-0.20195	-0.41891	-0.40804	-0.19325	-0.17039	-0.16837	-0.23532	-0.25017	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{9,100}^{\text{calc}}(\text{eV})$	0.14655	0.21747	0.17358	0.40696	0.12944	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{10,100}^{\text{calc}}(\text{eV})$	-0.12867	-0.31017	-0.30266	-0.10647	-0.10567	-0.10365	-0.22757	-0.14502	-0.10359	-0.10359	-0.15924	-0.10359	-0.10260	-0.10260
$E_{11,100}^{\text{calc}}(\text{eV})$	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{12,100}^{\text{calc}}(\text{eV})$	-33.62241	-67.47664	-66.57498	-33.59559	-32.67022	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$E_{13,100}^{\text{calc}}(\text{eV})$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{14,100}^{\text{calc}}(\text{eV})$	0	0	0	0	0	0	-13.59844	-13.59844	0	0	0	0	0	0
$E_{15,100}^{\text{calc}}(\text{eV})$	4.5263	8.70826	7.80660	4.12581	3.40044	12.49186	7.83016	3.32601	4.32754	4.32754	3.97398	4.17951	3.62128	3.91734

Table 15.121. The total bond energies of N-alkyl and N,N-dialkyl amides calculated using the functional group composition and the energies of Table 15.120 compared to the experimental values [3].

Formula	Name	C=O (f) Group	C-N (f) Group	NH Group	N-C (f) Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C14H29NO	N,N-Dimethylformamide	0	1	0	0	0	0	1	0	0	0	0	0	0	41.5142	41.5142	0.0000
C14H29NO	N,N-Dimethylacetamide	0	0	1	0	2	0	0	0	0	0	0	0	0	50.3142	50.3142	-0.0001
C14H29NO	N-Ethylacetamide	1	0	1	0	1	3	0	0	0	0	0	0	0	84.6349	84.6349	-0.0005



Table 15.122. The bond angle parameters of N-alkyl and N,N-dialkyl amides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}^\circ \text{AO})$ .

Angles of Angle	$2C_1'$ Bond 1 ( $\alpha_1$ )	$2C_2'$ Bond 2 ( $\alpha_2$ )	$2C_3'$ Terminal Atom 3 ( $\alpha_3$ )	$E_{\text{center}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$C_1$ Atom 1	$C_2$ Atom 2	$C_3$	$C_1$	$C_2$	$C_3$	$E_r$ (eV)	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle O C_1' N$ ( $C_1' = O$ (iii))	2.27954	2.64855	4.3243	16.17321 O	12	0.84115	0.84418		1	1	1	-1.44915			122.51	121.8 (N-methylacetamide)
$\angle C_1' C_2' N$ ( $C_1' = O$ (iii))	2.86175	2.64855	4.6904	-15.75493 C <sub>s</sub>	7	0.86359	0.9140 (Eq. (15.1.16))		1	1	1	-1.44915			116.63	114.1 (N-methylacetamide)
$\angle C_1' C_2' O$ ( $C_1' = O$ (iii))	2.86175	2.27954	4.5607	-16.68411 C <sub>s</sub>	24	0.81549	0.85395 (Eq. (15.1.14))		1	1	1	-1.6576			124.63	
$\angle C_1' N C_2'$ ( $C_1' = O$ (iii))	2.64855	2.80224	4.6904	-17.93127 C <sub>s</sub>	48	0.73878	0.83885		1	1	1	-1.83836			118.72	119.7 (N-methylacetamide)
Methyls $\angle H C_1' H$	2.11106	2.11106	3.4252	-15.75493	7	0.86359	1		1	1	0.75	0			108.44	107 (propane)
$\angle C_1' C_2' C_3'$													69.51			112 (propane) 113.8 (butane) 110.8 (isobutane) 111.0
$\angle C_1' C_2' H$																110.49 (butane) 111.4 (isobutane)
Main 1 $\angle H C_1' H$	2.09711	2.09711	3.4252	-15.75493	7	0.86359	1		1	1	0.75	0			109.50	108.5 (acetone)
$\angle C_1' C_2' C_3'$													70.56			109.44
$\angle C_1' C_2' H$													70.56			109.44
$\angle C_1' C_2' C_3'$ iso C <sub>s</sub>	2.91547	2.91547	4.7958	-16.68412 C <sub>s</sub>	25	0.81549	0.81549		1	1	1	-1.85856			110.67	110.8 (isobutane)
$\angle C_1' C_2' H$ iso C <sub>s</sub>	2.91547	2.11323	4.1633	-15.55033 C <sub>s</sub>	5	0.87495	0.91771		0.75	1	0.75	0			110.76	
$\angle C_1' C_2' H$ iso C <sub>s</sub>	2.91547	2.09711	4.1633	-15.55033 C <sub>s</sub>	5	0.87495	0.91771		0.75	1	0.75	0			111.27	111.4 (isobutane)
$\angle C_1' C_2' C_3'$ iso C <sub>s</sub>	2.90327	2.90327	4.7958	-15.55033 C <sub>s</sub>	5	0.87495	0.91771		0.75	1	0.75	-1.85836			111.27	111.4 (isobutane)
$\angle C_1' C_2' C_3'$													72.50			107.50



UREA ( $CH_4N_2O$ )

Urea,  $CH_4N_2O$ , comprises a  $C=O$  functional group and two  $C-NH_2$  moieties that each comprise a  $NH_2$  functional group and a  $C-N$  functional group. The  $C=O$  group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The  $NH_2$  and  $C-N$  functional groups are also equivalent to those given in the Amides section.  $E_r(atom-atom, msp^3.AO)$  (Eq. (15.52)) of the  $C=O$  and  $C-N$  groups are equivalent to those of formamide. The values given in the Amides section are  $-3.58557\text{ eV}$ , and  $-1.65376\text{ eV}$ , respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.79-15.108) are given in Table 15.128.

Table 15.123. The symbols of functional groups of urea.

Functional Group	Group Symbol
$C=O$ (urea)	$C=O$
$(O)C-N$ (urea)	$C-N$
$NH_2$ group	$NH_2$



Table 15.124. The geometrical bond parameters of urea and experimental values [1].

Parameter	C=O Group	C-N Group	NH <sub>2</sub> Group
$a$ ( $a_0$ )	1.290799	1.70920	1.32297
$c'$ ( $a_0$ )	1.13613	1.30736	0.97065
Bond Length $2c'$ ( $\text{\AA}$ )	1.20243	1.38365	1.02729
Exp. Bond Length ( $\text{\AA}$ )	1.212 (formamide)	1.368 (formamide)	1.027 (formamide) 1.022 (acetamide)
$h_{1c}$ ( $a_0$ )	0.61267	1.10098	0.89894
$e$	0.88018	0.76490	0.73369

Table 15.125. The MO to HO intercept geometrical bond parameters of urea.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{exp}^3, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy C2,sp <sup>3</sup> (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{Coulomb}}$ (eV) Final	$\bar{E}(\text{C2,sp}^3)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$H_1NC(O)N(H)-H$	N	-0.82688	0	0	0		0.93084	-15.65263		113.90	66.10	62.13	0.61843	0.5222
$H_1NC(O)-NH_2$	N	-0.82688	0	0	0		0.93084	-15.65263		103.93	76.07	50.02	1.09814	0.20922
$H_1NC(O)-NH_2$	C	-0.82688	-1.79278	-0.82688	0	-155.06223	0.91771	-18.27229	-18.08143	93.56	86.44	42.45	1.26106	0.04630
$H_1NC(NH_2)=O$	O	-1.79278	0	0	0		1.00000	-16.61853		137.10	42.90	63.45	0.53635	0.59978
$H_1NC_2(NH_2)=O$	C	-1.79278	-0.82688	-0.82688	0	-155.06223	0.91771	-18.27229	-18.08143	133.82	46.18	61.27	0.62034	0.51559



Table 15.126. The energy parameters (eV) of functional groups of urea.

Parameters	C = O Group	C - N Group	NH <sub>2</sub> Group
$n_1$	2	1	2
$n_2$	0	0	0
$n_3$	0	0	1
$C_1$	0.5	0.5	0.75
$C_2$	1	1	0.93613
$c_1$	1	1	0.75
$c_2$	0.85395	0.91140	1
$c_3$	2	0	0
$c_4$	4	2	1
$c_5$	0	0	2
$C_{1w}$	0.5	0.5	1.5
$C_{2w}$	1	1	1
$V_e$ (eV)	-112.61934	-38.24008	-78.77719
$V_p$ (eV)	23.95107	10.40705	28.03446
$T$ (eV)	43.62389	11.18655	29.77286
$V_m$ (eV)	-21.81195	-5.59327	-14.88643
$E(\text{AO} \text{HO})$ (eV)	0	-14.63489	-14.53414
$\Delta E_{H_2MO}(\text{AO} \text{HO})$ (eV)	-3.58557	-5.23932	-1.65376
$E_r(\text{AO} \text{HO})$ (eV)	3.58557	-9.39557	-12.88038
$E(n, \text{AO} \text{HO})$ (eV)	0	0	-14.53414
$E_r(H_2MO)$ (eV)	-63.27075	-31.63533	-48.73668
$E_r(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ (eV)	-3.58557	-1.65376	0
$E_r(MO)$ (eV)	-66.85630	-33.28912	-48.73660
$\omega$ ( $10^{15}$ rad / s)	19.9334	13.0822	59.4067
$E_K$ (eV)	13.12053	8.61093	39.10250
$\bar{E}_D$ (eV)	-0.23955	-0.19325	-0.39136
$\bar{E}_{Kvib}$ (eV)	0.21747 [32]	0.17358 [33]	0.40929 [22]
$\bar{E}_{osc}$ (eV)	-0.13081	-0.10647	-0.18672
$E_{moq}$ (eV)	0.11441	0.14803	0.14185
$E_r(\text{Group})$ (eV)	-67.11793	-33.39559	-49.11003
$E_{total}(c_1 \text{AO} \text{HO})$ (eV)	-14.63489	-14.63489	-14.53414
$E_{total}(c_2 \text{AO} \text{HO})$ (eV)	0	0	-13.59844
$E_D(\text{Group})$ (eV)	8.34955	4.12581	7.37901

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

Formula	Name	C = O Group	C - N Group	NH <sub>2</sub> Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>4</sub> N <sub>2</sub> O	Urea	1	2	2	31.35919	31.393	0.00108



Table 15.128. The bond angle parameters of urea and experimental values [1]. In the calculation of  $\theta_v$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

Angles of Angle	$2c'$ Bond 1 ( $a_v$ )	$2c'$ Bond 2 ( $a_v$ )	$2c'$ Terminal Atom ( $a_v$ )	$E_T$ Terminal Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c'_2$	$E_T$ (eV)	$\theta_v$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle HNH$	1.94130	1.94130	3.1464	-14.53414	N	0.93613 Eq. (15.62)	H	1	1	0.75	1.06823	0				108.27	
$\angle C'NH$	2.61473	1.94130	3.9328	-14.53414	N	0.93613 (Eq. (15.62))	C'	0.75	1	0.75	0.98033	0				118.61	119.2 (formamide)
$\angle OC'N$	2.27227	2.61473	4.3359	16.17521	12	0.84115	N	1	1	1	0.83596	-1.44915				124.91	125.0 (formamide)



# CARBOXYLIC ACID HALIDES ( $C_nH_{2n-1}OX$ , $X = F, Cl, Br, I$ ; $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl carboxylic acid halides,  $C_nH_{2n-1}OX$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. All carboxylic acid halides further comprise a  $C-X$  functional group where  $X$  is a halogen atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide  $C=O$  and  $C-C(O)$  groups are equivalent to those given in the Aldehydes section and the Ketones section, respectively. The values of  $E_r(atom-atom,msp^3.AO)$  given in these sections are  $-2.69893 eV$  and  $-1.44915 eV$ , respectively.

As in the case of alkyl halides, each  $(O)C-X$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $X$  AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the  $(O)C-Cl$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $C_2$  of Eq. (15.52) for the  $(O)C-Cl$ -bond MO given by Eq. (15.111) is  $C_2(C2sp^3HO \text{ to } Cl) = 0.81317$ . The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the  $C-Cl$  group of alkyl chlorides,  $E_r(atom-atom,msp^3.AO)$  of the  $(O)C-Cl$ -bond MO in Eq. (15.52) of alky carboxylic acid chlorides due to the charge donation from the  $C$  and  $Cl$  atoms to the MO is  $-1.44915 eV$  where both energy contributions



are given by Eq. (14.511). This matches the energy of the  $C - C(O)$  functional group with that of the  $(O)C - Cl$  group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)),  
5 and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs.  
10 (15.79-15.108) are given in Table 15.134.



Table 15.129. The symbols of functional groups of alkyl carboxylic acid chlorides.

Functional Group	Group Symbol
C-C(O)	C=O
C=O (alkyl carboxylic acid chloride)	C-Cl
O(C-Cl)	C-H (CH <sub>3</sub> )
CH <sub>3</sub> group	C-H (CH <sub>2</sub> )
CH <sub>2</sub> group	C-H
CH (alkyl) group	C-C (a)
CC bond (n-C)	C-C (b)
CC bond (iso-C)	C-C (c)
CC bond (tert-C)	C-C (d)
CC (iso to iso-C)	C-C (e)
CC (t to t-C)	C-C (f)
CC (t to iso-C)	

Table 15.130. The geometrical bond parameters of alkyl carboxylic acid chlorides and experimental values [1].

Parameter	C-C(O) Group	C=O Group	C-Cl Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\alpha$ (°)	2.04740	1.29007	2.32621	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$\alpha'$ (°)	1.43087	1.13977	1.69136	1.04856	1.05553	1.05861	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length												
2c' (Å)	1.51437	1.20628	1.79005	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.520 (acetone) 1.518 (2-butanone)	1.187 (acetyl chloride) 1.214 (acetic acid)	1.798 (acetyl chloride)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$\mu$ (°)	1.46439	0.62331	1.59705	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$\sigma$	0.69887	0.87757	0.72709	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides.  $R, R', R''$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}^2, \text{AO})$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $C2sp^2$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{calculated}}$ (eV) Final	$E(C2sp^2)$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$H_1C_1C_2(O)-Cl$	Cl	-0.72457	0	0	0	-154.41430	0.91771	-15.5033	-17.43350	69.62	110.38	30.90	1.99599	0.30463
$H_1C_1C_2(O)-Cl$	C	-1.34946	-0.72457	-0.72457	0	-154.41430	0.91771	-17.62436	-17.43350	54.69	125.31	23.23	2.13760	0.44625
$H_1C_1C_2(O)-O$	O	-1.34946	0	0	0	-154.41430	1.00000	-16.17521	-17.43350	137.27	42.73	66.31	0.52193	0.61784
$H_1C_1C_2(O)-O$	C	-1.34946	-0.72457	-0.72457	0	-154.41430	0.91771	-17.62436	-17.43350	134.28	45.72	62.45	0.60076	0.53901
$H_1C_1C_2(O)-Cl$	C	-0.72457	-1.34946	-0.72457	0	-154.41430	0.91771	-17.62436	-17.43350	59.30	120.70	26.96	1.82495	0.39408
$H_1C_1C_2(O)-Cl$	C	-0.72457	0	0	0	-152.34026	0.91771	-15.5033	-15.56407	73.62	106.38	34.98	1.67762	0.24675
$C-H(CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	-15.56407	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H(CH_3)$	C	-0.92918	-0.92918	0	0	-153.47006	0.91771	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H(CH_3)$ (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_1C_1C_2H_2CH_2-$ (C-C (a))	C	-0.92918	0	0	0	-152.54487	0.91771	-15.56407	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_1C_1C_2H_2CH_2-$ (C-C (a))	C	-0.92918	-0.92918	0	0	-153.47006	0.91771	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_1C_1C_2(H_1C_1'-R')HCH_2-$ (C-C (b))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_1C_1C_2(R''-H_2C_2')C_3(R''-H_2C_2')CH_2-$ (C-C (c))	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_1C_2(H_1C_1'-R')HCH_2-$ (C-C (d))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$isoC_1C_2(R''-H_2C_2')C_3(R''-H_2C_2')CH_2-$ (C-C (e))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$isoC_1C_2(H_1C_1'-R')HCH_2-$ (C-C (f))	C	-0.72457	-0.92918	-0.92918	0	-154.19663	0.91771	-17.40869	-17.21783	52.78	127.22	24.04	1.97443	0.47279
$isoC_1C_2(R''-H_2C_2')C_3(R''-H_2C_2')CH_2-$ (C-C (f))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.132. The energy parameters (eV) of functional groups of alkyl carboxylic acid chlorides.

Parameters	C-Cl(O) Group	C=O Group	C-Cl Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H (ii) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	2	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	0.81317	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.91771	0.85395	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	2	1	0	1	1	0	0	0	1	1	0
$C_6$	2	4	2	1	1	1	2	2	2	2	2	2
$C_7$	0	0	0	3	2	1	0	0	0	0	0	0
$C_8$	1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_9$	1	1	0.81317	1	1	1	1	1	1	1	1	1
$V_r$ (eV)	-30.19634	-111.25473	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_n$ (eV)	9.50874	23.87467	8.04332	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T$ (eV)	7.37432	42.82081	6.38036	32.33914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_n$ (eV)	-3.68716	-21.41040	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{(a)}(m)$ (eV)	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{(a)}(m)$ (eV)	0	-2.69893	-1.44915	0	0	0	0	0	0	0	0	0
$E_{(a)}(m)$ (eV)	-14.63489	2.69893	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{(a)}(m)$ (eV)	-31.63534	-63.27074	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{(a)}(m)$ (eV)	-1.44915	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{(a)}(m)$ (eV)	-33.08452	-65.96966	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^{15}$ rad/s)	16.4962	59.4034	7.42995	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$I_K$ (eV)	10.85807	39.10034	4.89052	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$I_n$ (eV)	-0.21568	-0.40804	-0.14475	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{K_{\alpha}}$ (eV)	0.14655	0.21077	0.09063	0.35532	0.35532	0.35532	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
$E_{K_{\alpha}}$ (eV)	[28]	[12]	[34]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[2]	[4]	[5]	[2]	[2]	[2]
$E_{K_{\alpha}}$ (eV)	-0.14240	-0.30266	-0.09943	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$F_{K_{\alpha}}$ (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$I_{(a)}(m)$ (eV)	-33.22692	-66.57498	-33.18395	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$I_{(a)}(m)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$I_{(a)}(m)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$I_{(a)}(m)$ (eV)	3.95714	7.80660	3.76614	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.133. The total bond energies of alkyl carboxylic acid chlorides calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3].

Formula	C-Cl(O) Group	C=O Group	C-Cl Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	CH Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>3</sub> ClO	1	1	1	1	0	0	0	0	0	0	0	0	28.03174	27.990	-0.00115



Table 15.134. The bond angle parameters of alkyl carboxylic acid chlorides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T = E_T(\text{atom} - \text{atom.msp}^2 \cdot \text{AO})$ .

Atoms of Angle	$2c^1$ Bond 1 ( $a_0$ )	$2c^2$ Bond 2 ( $a_0$ )	$2c^3$ Terminal Atoms ( $a_0$ )	$E_{\text{calc}}^{\text{calc}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{calc}}^{\text{calc}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$\zeta_2$	$E_T$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_l$ ( $^\circ$ )	$\theta_s$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C^1 C^2 O$	2.86175	2.27954	4.5926	-16.68411	24	-13.61806	O	0.81549	0.83395 (Eq. (15.113))	1	1	1	0.83472	-1.63376				125.70	
$\angle C^1 C^1 C^1$	2.86175	3.38271	5.1539	-15.75493	7	-12.96764 ( $C^1$ )	Cl	0.86359	0.86359	1	0.81317 (Eq. (15.111))	1	0.86359	-0.92918				110.98	111.6 (acetyl chloride)
$\angle C^1 C^1 C^1$	2.27954	3.38271	4.9841	-16.68412 ( $O$ )	25	-15.55033 ( $C^1$ )	5	0.81549	0.87495	1	0.81317 (Eq. (15.111))	1	0.84522	-0.92918				122.13	121.2 (acetyl chloride)
Methyl $\angle HC^1 H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C^1 C^1 C^1$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C^1 C^1 H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC^1 H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.6 (acetyl chloride) 108.5 (acetone)
$\angle C^1 C^1 C^1$															70.56			109.44	
$\angle C^1 C^1 H$															70.56			109.44	
$\angle C^1 C^1 C^1$	2.91547	2.91547	4.7958	-16.68412	25	-16.68412 $C^1$	25	0.81549	0.81549	1	1	1	0.81549	-1.85336				110.67	110.8 (isobutane)
$\angle C^1 C^1 H$	2.91547	2.11323	4.1633	-15.55033 $C^1$	5	-14.82575 $C^1$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C^1 C^1 H$	2.91547	2.09711	4.1633	-15.55033 $C^1$	5	-14.82575 $C^1$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C^1 C^1 C^1$	2.90327	2.90327	4.7958	-15.55033 $C^1$	5	-14.82575 $C^1$	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85336				111.27	111.4 (isobutane)
$\angle C^1 C^1 C^1$															72.50			107.50	



# CARBOXYLIC ACID ANHYDRIDES ( $C_nH_{2n-2}O_3$ , $n = 2, 3, 4, 5, \dots, \infty$ )

The alkyl carboxylic acid anhydrides,  $C_nH_{2n-2}O_3$ , have two  $(O)C-O$  moieties that each comprise  $C=O$  and  $C-O$  functional groups. The single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. The alkyl portion of the alkyl carboxylic acid anhydride may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride  $C=O$  and  $C-C(O)$  groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of  $E_r(atom-atom, msp^3.AO)$  given in these sections are  $-2.69893 eV$  and  $-1.44915 eV$ , respectively. The  $C-O$  group is also equivalent to that given in the Carboxylic Acid Esters section except that  $E_r(atom-atom, msp^3.AO)$  is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the  $C-O$  group,  $E_r(atom-atom, msp^3.AO)$  is  $-1.65376 eV$ . It is based on the energy match between the  $O$  AO and the  $C2sp^3$  HO of each  $C-C(O)$  group and is given by the linear combination of  $-0.72457 eV$  (Eq. (14.151)) and  $-0.92918 eV$  (Eq. (14.513)), respectively. This matches  $-0.72457 eV$ , the energy contribution of each of the  $C2sp^3$  HOs to each  $C-C(O)$  functional group, with that of the corresponding energy component of the  $C-O$  group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl



carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.79-15.108) are given in Table 15.140.



Table 1.5.135. The symbols of functional groups of alkyl carboxylic acid anhydrides.

Functional Group	Group Symbol
C-C(O)	C-C(O)
C=O	C=O
(O)C-O	C-O
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH (alkyl) group	C-H
CC bond (n-C)	C'-C' (a)
CC bond (iso-C)	C'-C' (b)
CC bond (tert-C)	C'-C' (c)
CC (iso to iso-C)	C'-C' (d)
CC (1 to 1-C)	C'-C' (e)
CC (1 to iso-C)	C'-C' (f)

Table 1.5.136. The geometrical bond parameters of alkyl carboxylic acid anhydrides and experimental values [1].

Parameter	C-C(O) Group	C=O Group	C-O Group	C-H (CH <sub>3</sub> ) Group	C'-H (CH <sub>3</sub> ) Group	C'-C' (a) Group	C'-C' (b) Group	C'-C' (c) Group	C'-C' (d) Group	C'-C' (e) Group	C'-C' (f) Group
$a$ (Å)	2.04740	1.25907	1.73490	1.64920	1.67122	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.45087	1.13977	1.31716	1.04856	1.05553	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.51437	1.20638	1.39402	1.10974	1.11713	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.520 (acetone) 1.518 (2-butanone)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.532 (propane) 1.531 (isobutane)	1.532 (propane) 1.531 (isobutane)	1.532 (propane) 1.531 (isobutane)	1.532 (propane) 1.531 (isobutane)	1.532 (propane) 1.531 (isobutane)	1.532 (propane) 1.531 (isobutane)
$b_1 c'$ (Å)	1.46459	0.62331	1.12915	1.27295	1.29569	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.69887	0.87737	0.75921	0.63380	0.63159	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.137. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides.  $R, R', R''$  are  $H$  or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{map}^3, \text{AO})$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy C2sp <sup>3</sup> (eV)	$r_{\text{final}}$ (a <sub>0</sub> )	$r_{\text{initial}}$ (a <sub>0</sub> )	$E_{\text{electron}}$ (eV) Final	$E(\text{C2sp}^3)$ (eV) Final	$\theta'$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
$RC_1H_2C_2(O) - O_n - C_n(O)C_1H_2R'$	$O_n$	-0.82688	-0.82688	0	0	-154.51660	0.82562	1.00000	-16.47951	-17.53580	98.32	81.68	46.34	1.19766	0.11949
$RC_1H_2C_2(O) - O_n - C_n(O)C_1H_2R'$	$C_n$	-0.82688	-1.34946	-0.82688	0	-154.51660	0.76753	0.91771	-17.72667	-17.53580	93.21	86.79	42.74	1.27417	0.04298
$RC_1H_2[R(C_1H_2C_2(O)O)C_n]C_n = O_n$	$O_n$	-1.34946	0	0	0	-154.51660	0.84115	1.00000	-16.17521	-17.53580	137.27	42.73	66.31	0.32193	0.61784
$RC_1H_2[R(C_1H_2C_2(O)O)C_n]C_n = O_n$	$C_n$	-1.34946	-0.72457	-0.82688	0	-154.51660	0.76753	0.91771	-17.72667	-17.53580	134.08	45.92	62.20	0.60283	0.33394
$RH_2C_n - C_n(O)OC_n(O)C_1H_2R'$	$C_n$	-0.72457	-1.34946	-0.82688	0	-154.51660	0.76753	0.91771	-17.72667	-17.53580	58.35	121.45	26.56	1.83135	0.40045
$H_1C_n - C_n(O)OC_n(O)C_1H_2R'$	$C_n$	-0.72457	0	0	0	-152.34026	0.87495	0.91771	-15.55033	-15.55946	73.62	106.58	34.98	1.67762	0.24675
$RH_2C_n - C_n(O)OC_n(O)C_1H_2R'$	$C_n$	-0.72457	-0.92918	0	0	-153.20945	0.82362	0.91771	-16.47951	-16.28865	67.40	112.60	31.56	1.74821	0.31734
$C' - H(C'H_2)$	$C'$	-0.92918	0	0	0	-152.54487	0.86359	0.91771	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C' - H(C'H_2)$	$C'$	-0.92918	-0.92918	0	0	-153.47406	0.81549	0.91771	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C' - H(C'H_2)$ (ii)	$C'$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.77247	0.91771	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_1C_1C_2H_2C_1H_2 -$ (C'-C' (aa))	$C_n$	-0.92918	0	0	0	-152.54487	0.86359	0.91771	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_1C_1C_2H_2C_1H_2 -$ (C'-C' (aa))	$C_n$	-0.92918	-0.92918	0	0	-153.47406	0.81549	0.91771	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R - H_1C_1C_2H_2C_1H_2 -$ (C'-C' (bb))	$C_n$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.77247	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_1C_1C_2H_2C_1H_2 -$ (C'-C' (bb))	$C_n$	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.75889	0.91771	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_1C_2H_2C_1H_2 -$ (C'-C' (cc))	$C_n$	-0.92918	-0.92918	-0.92918	0	-154.40324	0.77247	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$isoC_1C_2H_2C_1H_2 -$ (C'-C' (cc))	$C_n$	-0.92918	-0.72457	-0.72457	-0.72457	-154.51399	0.76765	0.91771	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$isoC_1C_2H_2C_1H_2 -$ (C'-C' (cc))	$C_n$	-0.72457	-0.72457	-0.92918	0	-154.19605	0.78155	0.91771	-17.40869	-17.21763	52.78	127.22	24.04	1.92443	0.47279
$isoC_1C_2H_2C_1H_2 -$ (C'-C' (ff))	$C_n$	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.76765	0.91771	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.138. The energy parameters (eV) of functional groups of alkyl carboxylic acid anhydrides.

Parameters	C-C (O)	C=O	C-O	C-H <sub>3</sub>	C-H <sub>2</sub>	C-H (H)	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
$\eta_1$	1	2	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.91771	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	2	0	0	1	1	0	0	0	1	1	0
$C_6$	2	4	2	1	1	1	2	2	2	2	2	2
$C_7$	0	0	0	3	2	1	0	0	0	0	0	0
$C_8$	1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_9$	1	1	1	1	1	1	1	1	1	1	1	1
$C_{10}$	-30.19634	-111.25473	-35.08488	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
$V_1$ (eV)	9.50874	23.87467	10.32968	38.92728	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
$V_2$ (eV)	7.37432	42.82081	10.11150	32.53914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
$V_3$ (eV)	-3.68716	-21.41040	-5.05575	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
$E_1$ (eV)	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,10}$ (eV)	0	-2.69893	-2.69893	0	0	0	0	0	0	0	0	0
$E_2$ (eV)	-14.63489	2.69893	-11.93596	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_3$ (eV)	-31.63534	-63.27074	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$E_4$ (eV)	-1.44915	-2.69893	-1.63376	0	0	0	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836
$E_5$ (eV)	-33.08452	-65.96966	-33.28912	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\omega$ (10 <sup>6</sup> rad/s)	16.4962	59.4034	24.3637	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.43699	9.43699
$E_6$ (eV)	10.85807	39.10034	16.03660	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
$E_7$ (eV)	-0.21568	-0.40804	-0.26373	-0.25532	-0.25017	-0.24966	-0.16315	-0.16315	-0.16315	-0.16315	-0.16315	-0.16315
$E_8$ (eV)	0.14655	0.21077	0.13638	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
$E_9$ (eV)	[28]	[12]	[35]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[2]	[4]	[5]	[2]	[2]	[2]
$E_{10}$ (eV)	-0.14240	-0.30266	-0.19554	-0.22737	-0.14502	-0.07200	-0.10359	-0.07200	-0.15924	-0.10359	-0.10359	-0.10359
$E_{11}$ (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{12}$ (eV)	-33.22692	-66.57498	-33.48466	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.59732	-33.59732
$E_{13}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{14}$ (eV)	0	0	0	-15.59844	-15.59844	-15.59844	0	0	0	0	0	0
$E_{15}$ (eV)	3.95714	7.80660	4.21488	12.49186	7.83016	3.52601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.139. The total bond energies of alkyl carboxylic acid anhydrides calculated using the functional group composition and the energies of Table 15.138 compared to the experimental values [3].

Formula	Name	C-C (O)	C=O	C-O	C-H <sub>3</sub>	C-H <sub>2</sub>	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic anhydride	2	2	2	2	2	0	0	0	0	0	0	0	56.94096	56.948	0.00013
C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	Propanoic anhydride	2	2	2	2	2	0	0	0	0	0	0	0	81.25636	81.401	0.00177







NITRILES ( $C_nH_{2n-1}N$ ,  $n = 2, 3, 4, 5 \dots \infty$ )

The nitriles,  $C_nH_{2n-1}N$ , comprise a  $C \equiv N$  functional group, and the single bond of carbon to the nitrile carbon atom,  $C - CN$ , is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and  
 5 may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C - C$  bonds can be identified. The n-alkane  $C - C$  bond is the same as that of straight-chain alkanes. In addition, the  $C - C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl  
 10 to t-butyl, and t-butyl to t-butyl  $C - C$  bonds comprise functional groups. The branched-chain-alkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile  $C \equiv N$  is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for  $\Delta E_{H_2MO}(AO/HO)$  is two times that given in Eq. (14.343),  
 16.20002 eV, in order to match the  $N$  AOs to that of the nitrile  $C2sp^3$  HO having a bond order  
 15 of three.  $E_T(atom - atom, msp^3.AO)$  of the  $C \equiv N$  functional group is  $-1.56513$  eV (Eq. (14.342)) corresponding to the third-order bonded  $C2sp^3$  HO.

The  $C - CN$  functional group is equivalent to that of an alkyl  $C - C$  group given in the Continuous-Chain Alkanes section except that  $E_T(H_2MO)$  and  $\bar{E}_{Kvib}$  are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section,  $E_T(atom - atom, msp^3.AO)$  of the  
 20 alkyl  $C - C$  group is  $-1.85836$  eV where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded  $C2sp^3$  HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each  $E_D(group)$  of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the



$E_D(\text{group})$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of nitriles determined using Eqs. (15.79-15.108) are given in Table 15.146. The C of the  $C \equiv N$  group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes.



Table 15.141. The symbols of functional groups of nitriles.

Functional Group	Group Symbol
C-CN	C-C (i)
CN	C≡N
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH (alkyl) group	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.142. The geometrical bond parameters of nitriles and experimental values [1].

Parameter	C-C (i) Group	C≡N Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\alpha$ (°)	1.91255	1.20590	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$\alpha'$ (°)	1.38295	1.09813	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length	1.46365	1.16221	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.468 (acetonitrile)	1.159 (acetonitrile)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h_{\text{C}}$ (°)	1.382110	0.49828	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$\epsilon$	0.72309	0.91064	0.63380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.143. The MO to HO intercept geometrical bond parameters of nitriles.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{usp}^3, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy ( $\text{C}2\text{sp}^3$ ) (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{bond}}$ ( $a_0$ )	$E_{\text{calculated}}$ (eV) Final	$E(\text{C}2\text{sp}^3)$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$RH_2C_2C_2N$	N	-0.78257	0	0	0	-153.32744	0.93084	0.87170	-15.60832	-	147.01	32.99	72.28	0.36099	0.73114
$RH_2C_2C_2N$	C <sub>n</sub>	-0.78257	-0.92918	0	0	-153.32744	0.91771	0.82272	-16.37350	-16.34664	145.42	34.58	69.58	0.42077	0.67756
$RH_2C_2C_2N$	C <sub>n</sub>	-0.92918	-0.78257	0	0	-153.32744	0.91771	0.82272	-16.37350	-16.34664	81.32	98.68	38.00	1.50718	0.12023
$H_2C_2C_2N$	C <sub>n</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	83.50	94.50	40.67	1.45066	0.06771
$RH_2C_2C_2C_2N$	C <sub>n</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.60325	80.53	99.47	37.51	1.51718	0.13423
$C-H$ (CH <sub>3</sub> )	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH <sub>3</sub> )	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.60325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH <sub>3</sub> ) (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37226
$H_2C_2C_2H_2CH_2-$ (C-C (a))	C <sub>n</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.68	1.83879	0.38106
$H_2C_2C_2H_2CH_2-$ (C-C (a))	C <sub>n</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.60325	56.41	123.59	26.06	1.90090	0.45117
$R-H_2C_2C_2(H_2C_2-R')HCH_2-$ (C-C (b))	C <sub>n</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2C_2(R'-H_2C_2)C_2(R''-H_2C_2)CH_2-$ (C-C (c))	C <sub>n</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.73889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_2C_2(H_2C_2-R')HCH_2-$ (C-C (d))	C <sub>n</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_2C_2(R'-H_2C_2)C_2(R''-H_2C_2)CH_2-$ (C-C (e))	C <sub>n</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.67655	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_2C_2(H_2C_2-R')HCH_2-$ (C-C (f))	C <sub>n</sub>	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_2C_2(R'-H_2C_2)C_2(R''-H_2C_2)CH_2-$ (C-C (f))	C <sub>n</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.67655	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.144. The energy parameters (eV) of functional groups of nitriles.

Parameters	C-C (f) Group	C-N Group	C-H <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$n_1$	1	3	2	1	1	1	1	1	1	1
$n_2$	0	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1
$C_4$	0.91771	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	1	0	1	0	0	0	1	1	0
$C_6$	2	6	1	1	2	2	2	2	2	2
$C_7$	0	0	3	1	0	0	0	0	0	0
$C_{10}$	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{20}$	1	1	1	1	1	1	1	1	1	1
$V'_e$ (eV)	-33.01231	-207.49229	-107.32728	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V'_p$ (eV)	9.83824	37.16984	38.92728	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T$ (eV)	8.63043	86.03250	32.53914	21.06675	10.48582	6.77464	6.90500	6.77464	6.90500	6.90500
$V'_m$ (eV)	-4.31522	-43.01625	-16.26957	-10.53337	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E'_{(100\text{ m})}$ (eV)	-14.63489	32.40004	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E'_{(100\text{ m})}$ (eV)	-1.85837	0	0	0	0	0	0	0	0	0
$E'_T$ (eV)	-12.77652	32.40004	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E'_T$ (eV)	-31.63537	-94.90616	-67.69451	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$E'_T$ (atom - atom, msp <sup>3</sup> , AO) (eV)	-1.85836	-1.56513	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E'_T$ (100) (eV)	-33.49374	-96.47124	-67.69450	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\omega$ (10 <sup>4</sup> rad/s)	19.2516	22.0753	24.9286	24.1759	9.43699	9.43699	15.4846	9.43699	15.4846	9.43699
$E'_K$ (eV)	12.67172	14.53031	16.40846	15.91299	6.21159	6.21159	10.19220	6.21159	10.19220	6.21159
$E'_D$ (eV)	-0.23588	-0.24250	-0.25352	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.20896	-0.16515
$E'_{K10}$ (eV)	0.11407	0.28107	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.09944	0.12312
$E'_{K10}$ (Eq. (13.458))	[37]	[37]	(Eq. (13.458))	(Eq. (13.458))	[2]	[4]	[5]	[2]	[5]	[2]
$E'_{K10}$ (Eq. (13.458))	-0.17884	-0.10197	-0.22757	-0.14502	-0.10359	-0.07526	-0.15924	-0.10359	-0.15924	-0.10359
$E'_{K10}$ (Eq. (13.458))	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E'_T$ (Eq. (13.458))	-33.67258	-96.77713	-67.92207	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.24376	-33.59732
$E'_{K10}$ (Eq. (13.458))	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E'_{K10}$ (Eq. (13.458))	0	0	-13.59844	-13.59844	0	0	0	0	0	0
$E'_{K10}$ (Eq. (13.458))	4.40280	8.82594	12.49186	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734







# THIOLS ( $C_nH_{2n+2}S_m$ , $n=1,2,3,4,5\ldots\infty$ )

The alkyl thiols,  $C_nH_{2n+2}S_m$ , comprise a  $SH$  functional group and a  $C-S$  functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the  $SH$  functional group is solved using Eq. (15.41). As in the case of the  $C-H$  bonds of  $CH_n$ ,  $n=1,2,3$ , the  $S-H$ -bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the  $S3p$  shell. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $S3p$  shell and comprises 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of  $S$ ,  $E(S) = -10.36001 \text{ eV}$ , is less than that of  $H$ , the linear combination of the  $H_2$ -type ellipsoidal MO with the  $S3p$  shell further comprises an excess 50% charge-density donation from  $H$  to the  $S3p$  shell of the  $S-H$ -bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four  $3p$  electrons. From Eq. (15.12), the sum  $E_T(S, 3p)$  of the energies of  $S$ ,  $S^+$ ,  $S^{2+}$ , and  $S^{3+}$  [38] is

$$\begin{aligned} E_T(S, 3p) &= 10.36001 \text{ eV} + 23.33788 \text{ eV} + 34.79 \text{ eV} + 47.222 \text{ eV} \\ &= 115.70989 \text{ eV} \end{aligned} \quad (15.118)$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{3p}$  of the  $S3p$  shell may be calculated from the Coulombic energy using Eqs. (15.13) and (15.118):

$$r_{3p} = \sum_{q=12}^{15} \frac{(Z-q)e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} = \frac{10e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} = 1.17585a_0 \quad (15.119)$$

where  $Z=16$  for sulfur. Using Eqs. (15.14) and (15.119), the Coulombic energy  $E_{Coulomb}(S, 3p)$  of the outer electron of the  $S3p$  shell is



$$E_{Coulomb}(S, 3p) = \frac{-e^2}{8\pi\epsilon_0 r_{3p}} = \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} = -11.57099 \text{ eV} \quad (15.120)$$

The sharing of the electrons between the  $S$  and  $H$  atoms permits the formation an  $S-H$ -bond MO that is lowered more in energy than the participating  $S3p$  orbital which consequently increases in energy. By considering the 50% electron redistribution in the  $S-H$  group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{S-H3p}$  of the  $S3p$  shell may be calculated from the Coulombic energy using Eq. (15.18)

$$\begin{aligned} r_{S-H3p} &= \left( \sum_{n=12}^{15} (Z-n) + 0.25 \right) \frac{e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} \\ &= \frac{10.5e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} \\ &= 1.23465a_0 \end{aligned} \quad (15.121)$$

where the  $s = -1$  in Eq. (15.18) due to the charge donation from  $H$  to  $S$ . Using Eqs. (15.19) and (15.121), the Coulombic energy  $E_{Coulomb}(S_{S-H}, 3p)$  of the outer electron of the  $S3p$  shell is

$$\begin{aligned} E_{Coulomb}(S_{S-H}, 3p) &= \frac{-e^2}{8\pi\epsilon_0 r_{S-H3p}} \\ &= \frac{-e^2}{8\pi\epsilon_0 1.23465a_0} \\ &= -11.01999 \text{ eV} \end{aligned} \quad (15.122)$$

Thus,  $E_r(S-H, 3p)$ , the energy change of each  $S3p$  shell with the formation of the  $S-H$ -bond MO is given by the difference between Eq. (15.120) and Eq. (15.122):

$$\begin{aligned} E_r(S-H, 3p) &= E(S_{S-H}, 3p) - E(S, 3p) \\ &= -11.01999 \text{ eV} - (-11.57099 \text{ eV}) \\ &= 0.55100 \text{ eV} \end{aligned} \quad (15.123)$$

15 Then, in Eq. (15.42):

$$\begin{aligned} E_r(AO / HO) &= E(S) - E_r(S-H, 3p) \\ &= -10.36001 \text{ eV} - 0.55100 \text{ eV} \\ &= -10.91101 \text{ eV} \end{aligned} \quad (15.124)$$

And, in Eq. (15.56),

$$E_r(atom - atom, msp^3 AO) = 0.55100 \text{ eV} \quad (15.125)$$



Due to the charge donation from  $H$  to  $S$ ,  $c_1 = 1$  in both Eqs. (15.42) and (15.56). As in the case of the  $C-H$ -bond MO,  $C_1 = 0.75$  based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is also one, and the energy matching condition is  
 5 determined by the  $C_2$  parameter. Using the energy of  $S$ ,  $E(S) = -10.36001 \text{ eV}$  in Eq. (15.65), the hybridization factor  $C_2$  of Eq. (15.52) for the  $S-H$ -bond MO is

$$C_2(S3p \text{ to } H) = \frac{E(S, 3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144 \quad (15.126)$$

Since the energy of  $S$  is matched to the Coulombic energy between the electron and proton of  $H$ ,  

$$E(H(a_0)), \quad E_{\text{initial}}(c_s \text{ AO/HO}) = E(H(a_0)) = -13.60580 \text{ eV},$$
  
 10  $E_{\text{initial}}(c_s \text{ AO/HO}) = E(H) = -13.59844 \text{ eV}$ , and  $E_{\text{mag}}$  is that corresponding to  $E(H(a_0))$  given by Eq. (15.58).  $E_D(\text{Group})$  for hydrogen sulfide is equivalent to that of the  $SH$  functional group, and the  $E_D(\text{Group})$  (eV) for dihydrogen sulfide follows the same derivation as that for the  $SH$  functional group except that the parameters correspond to  $n_1 = 2$  rather than  $n_1 = 1$  in Eqs. (15.42) and (15.56).

15 Furthermore, with the energy of  $S$  matched to the Coulombic energy between the electron and proton of  $H$ , the energy of the  $C-S$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with  $E(\text{AO/HO}) = 0$  and  $E_T(\text{AO/HO}) = \Delta E_{H_2 \text{ MO}}(\text{AO/HO})$ . Then, the solution of the  $C-S$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of  $C$  to form a single  $2sp^3$  shell as an  
 20 energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $S$  AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243),  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then,  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a  
 25 corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $S$  AO has an energy of  $E(S) = -10.36001 \text{ eV}$ . To meet the equipotential condition of the union of the



$C-S$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.51) for the  $C-S$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } S) = \frac{E(S)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.64965 \quad (15.127)$$

Since the sulfur is energy matched to  $E(H(a_0))$  in the  $S-H$ -bond MO,

5  $E_T(atom - atom, msp^3.AO)$  of the  $C-S$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $S$  atoms to the MO is  $-0.72457 \text{ eV}$  corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and  
10 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted  
15 from the weighted sum of the  $E_D(Group)$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The  $C-C$  bonds to the  $HCSH$  group (one  $H$  bond to  $C$ ) were each treated as an iso  $C-C$  bond. The  $C-C$  bonds to the  $CSH$  group (no  $H$  bonds to  $C$ ) were each treated as a tert-butyl  $C-C$ .  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.79-15.108) are given in Table 15.152.



Table 15.147. The symbols of functional groups of alkyl thiols.

Functional Group	SH Group Symbol
SH group	SH
H <sub>2</sub> S	H <sub>2</sub> S
C-S	C-S
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.148. The geometrical bond parameters of alkyl thiols and experimental values [1].

Parameter	S-H (H <sub>2</sub> S)	SH Group	C-S Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\alpha$ (°)	1.83762	1.83762	1.90975	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$\alpha'$ (°)	1.26842	1.26842	1.71455	1.04856	1.05535	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (Å)	1.34244	1.34244	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.3556 (hydrogen sulfide)	1.34066 (methanethiol)	1.819 (ethanethiol)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
$b, c$ (°)	1.32964	1.32964	0.84112	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.69025	0.69025	0.89778	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.149. The MO to HO intercept geometrical bond parameters of alkyl thiols.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{resp. } A.O.)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{total}}^{\text{bond}}$ (eV) Final	$E(C2sp^3)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
S-H (hydrogen sulfide)	S	0.55100	0	0	0		1.32010	1.23465	-11.01999		108.65	71.35	61.62	0.87355	0.39487
RS-H (dihydrogen sulfide)	S	-0.30229	0.55100	0	0		1.32010	0.92955	-14.63704		87.09	92.91	44.28	1.31557	0.04714
C-H <sub>3</sub> -SH	S	-0.30229	0.55100	0	0		1.32010	0.92955	-14.63704		132.06	47.94	55.13	1.09181	0.62274
C <sub>2</sub> H <sub>5</sub> -SH	C	-0.30229	0	0	0	-151.97798	0.91771	0.89382	-15.18804	-14.99117	69.84	110.16	88.87	0.03762	1.67692
RC <sub>2</sub> H <sub>4</sub> C <sub>2</sub> H <sub>4</sub> -C <sub>2</sub> H <sub>4</sub> SH	C	-0.30229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.32765
C-H (CH <sub>3</sub> )	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
C-H (CH <sub>2</sub> )	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
C-H (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
H <sub>3</sub> C <sub>2</sub> C <sub>2</sub> H <sub>4</sub> CH <sub>2</sub> - (C-C (e))	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
H <sub>3</sub> C <sub>2</sub> C <sub>2</sub> H <sub>4</sub> CH <sub>2</sub> - (C-C (e))	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
R-H <sub>3</sub> C <sub>2</sub> C <sub>2</sub> H <sub>4</sub> CH <sub>2</sub> - (C-C (e))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
R-H <sub>3</sub> C <sub>2</sub> C <sub>2</sub> H <sub>4</sub> CH <sub>2</sub> - (C-C (e))	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.73889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50370
isoC <sub>2</sub> H <sub>5</sub> (H <sub>3</sub> C <sub>2</sub> -R)HCH <sub>2</sub> - (C-C (e))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
isoC <sub>2</sub> H <sub>5</sub> (R'-H <sub>3</sub> C <sub>2</sub> )C <sub>2</sub> (R'-H <sub>3</sub> C <sub>2</sub> )CH <sub>2</sub> - (C-C (e))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
isoC <sub>2</sub> H <sub>5</sub> (H <sub>3</sub> C <sub>2</sub> -R)HCH <sub>2</sub> - (C-C (e))	C	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.93445	0.47279
isoC <sub>2</sub> H <sub>5</sub> (R'-H <sub>3</sub> C <sub>2</sub> )C <sub>2</sub> (R'-H <sub>3</sub> C <sub>2</sub> )CH <sub>2</sub> - (C-C (e))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table I.5.150. The energy parameters (eV) of functional groups of alkyl thiols.

Parameters	$H_{1s}$	$SH$	$C-S$	$C-H$	$C-H_2$	$C-C$	$C-C$	$C-C$	$C-C$	$C-C$	$C-C$
	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
$H_1$	2	1	1	1	2	1	1	1	1	1	1
$H_2$	0	0	0	0	1	0	0	0	0	0	0
$H_3$	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.75	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5
$C_2$	0.76144	0.76144	0.64965	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1
$C_4$	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	2	1	0	0	1	1	0	0	1	1	0
$C_6$	1	1	2	1	1	1	2	2	2	2	2
$C_7$	1	1	0	1	2	1	0	0	0	0	0
$C_8$	0.75	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5
$C_9$	0.76144	0.76144	0.64965	1	1	1	1	1	1	1	1
$C_{10}$	-72.80662	-36.40331	-46.36495	-107.32728	-70.41425	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
$V_1$ (eV)	21.43310	10.72655	7.93551	38.92728	25.78002	12.87680	9.33552	9.33552	9.33552	9.33552	9.33552
$V_2$ (eV)	19.81003	9.90502	12.13899	32.53914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464
$V_3$ (eV)	-9.90502	-4.95251	-6.00949	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
$E_{1st}^{ion} (eV)$	-20.72002	-10.36001	0	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1st}^{ion} (eV)$	1.10200	0.55100	-0.72457	0	0	0	0	0	0	0	0
$E_1^{1st} (eV)$	-19.61802	-10.91101	0.72457	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_2^{1st} (eV)$	-63.27032	-31.63526	-31.63537	-67.69451	-49.66493	-31.63553	-31.63557	-31.63557	-31.63557	-31.63557	-31.63557
$E_3^{1st} (eV)$	1.10200	0.55100	-0.72457	0	0	0	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836
$E_4^{1st} (eV)$	-62.16874	-31.08437	-32.35904	-67.69450	-49.66493	-31.63557	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\omega$ ( $10^5$ rad/s)	12.5415	12.5415	30.5436	24.9286	24.2751	24.1759	6.21159	6.21159	6.21159	6.21159	6.21159
$E_K$ (eV)	8.25504	8.25504	20.10434	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.21159
$E_{1st}^{ion}$ (eV)	-0.17669	-0.17669	-0.28705	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515
$E_{2nd}^{ion}$ (eV)	0.32422	0.32422	0.08146	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312
$E_{3rd}^{ion}$ (eV)	-0.01458	-0.01458	-0.24632	-0.22757	-0.14502	-0.07200	-0.10559	-0.10559	-0.10559	-0.10559	-0.10559
$E_{4th}^{ion}$ (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{5th}^{ion}$ (eV)	-31.10493a	-31.09296	-32.60626	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$E_{6th}^{ion}$ (eV)	-13.60580	-13.60580	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{7th}^{ion}$ (eV)	-13.59844	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0
$E_{8th}^{ion}$ (eV)	3.78628	3.77430	3.33648	12.49186	7.83016	3.32601	4.32754	4.29921	4.29921	4.29921	4.29921
$E_{9th}^{ion}$ (eV)	-31.09296 eV	-31.09296 eV	-31.09296 eV	-31.09296 eV	-31.09296 eV	-31.09296 eV	-31.09296 eV	-31.09296 eV	-31.09296 eV	-31.09296 eV	-31.09296 eV

a  $E_{1st}^{ion} (n=1,2,3) = E_1 (n=1) - E_2 (n=1) = 62.19789$  eV  $- (-31.09296$  eV).



Table 15.151. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values [3]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_p(\text{core})$  ( $\text{eV}$ ) values base composition is given by (15.58).

Formula	Name	$H_2S$ Group	$SH$ Group	$C-S$ Group	$CH_3$	$CH_2$	$CH$	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	$E_{\text{mag}}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$HS$	Hydrogen Sulfide	1	1	0	0	0	0	0	0	0	0	0	0	0	3.633	3.633	-0.0320
$CH_3S$	Methylthiol	0	1	0	0	0	0	0	0	0	0	0	0	0	7.5038	7.603	0.0082
$CH_3CH_2S$	Ethylthiol	0	1	0	1	0	0	0	0	0	0	0	0	0	19.0264	19.575	-0.00141
$CH_3CH_2CH_2S$	1-Propanethiol	0	1	0	1	1	0	0	0	0	0	0	0	0	31.7694	31.762	0.00005
$CH_3CH_2CH_2CH_2S$	2-Propanethiol	0	1	0	2	0	0	0	0	0	0	0	0	0	43.91804	43.933	0.00035
$CH_3CH_2CH_2CH_2CH_2S$	1-Butanethiol	0	1	0	2	1	0	0	0	0	0	0	0	0	56.0274	56.089	0.00024
$CH_3CH_2CH_2CH_2CH_2CH_2S$	2-Butanethiol	0	1	0	3	0	0	0	0	0	0	0	0	0	68.14830	68.181	0.00009
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2S$	2-Methyl-1-propanethiol	0	1	0	2	1	1	0	0	0	0	0	0	0	80.39114	80.461	0.00094
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	2-Methyl-2-propanethiol	0	1	0	3	0	0	0	0	0	0	0	0	0	92.54884	92.570	0.00025
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	2-Methyl-1-butanethiol	0	1	0	3	1	0	0	0	0	0	0	0	0	104.70000	104.700	0.00000
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	1-Pentanethiol	0	1	0	4	0	0	0	0	0	0	0	0	0	116.83344	116.834	-0.00004
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	2-Methyl-2-butanethiol	0	1	0	4	1	0	0	0	0	0	0	0	0	128.96677	128.967	-0.00002
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	3-Methyl-2-butanethiol	0	1	0	5	0	0	0	0	0	0	0	0	0	141.09995	141.100	-0.00005
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	2,2-Dimethyl-1-propanethiol	0	1	0	3	1	0	0	0	0	0	0	0	0	153.23257	153.233	-0.00003
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	1-Hexanethiol	0	1	0	5	0	0	0	0	0	0	0	0	0	165.36592	165.366	-0.00004
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	2-Methyl-2-pentanethiol	0	1	0	6	0	0	0	0	0	0	0	0	0	177.49927	177.500	-0.00003
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	2,3-Dimethyl-2-butanethiol	0	1	0	6	1	0	0	0	0	0	0	0	0	189.63262	189.633	-0.00004
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	1-Heptanethiol	0	1	0	6	0	0	0	0	0	0	0	0	0	201.76597	201.766	-0.00003
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	1-Octanethiol	0	1	0	7	0	0	0	0	0	0	0	0	0	213.89932	213.900	-0.00004
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$	1-Decanethiol	0	1	0	9	0	0	0	0	0	0	0	0	0	226.03267	226.033	-0.00004

Table 15.152. The bond angle parameters of alkyl thiols and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

Atoms of Angle	$2c_1$ Bond 1 ( $\theta_1$ )	$2c_2$ Bond 2 ( $\theta_2$ )	$2c_3$ Terminal Atoms ( $\theta_3$ )	$E_{\text{calc}}$ Atom 1	$E_{\text{calc}}$ Atom 2	$F_{\text{calc}}$ Atom 1	$F_{\text{calc}}$ Atom 2	$C_1$	$C_2$	$C_3$	$\theta_1$ (°)	$\theta_2$ (°)	$\theta_3$ (°)	$\theta_4$ (°)	$E_T$ (eV)	$C-C$ (f)	$E_{\text{mag}}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$ZHX$	2.53685	3.42910	4.3166	-10.36001	-15.75493	0.76144	0.86359	0.75	1	0.75	97.28	97.28	97.28	97.28	0	0	0	3.633	3.633	-0.0320
$ZC_1C_2S$	2.91547	3.42910	3.2544	-16.68412	-10.36001	0.81549	0.86359	1	0.6965	0.75	109.44	109.44	109.44	109.44	-0.72457	0	0	7.5038	7.603	0.0082
$ZHC_2H$	2.11106	2.11106	3.4252	-15.75493	-15.75493	0.86359	0.86359	1	1	0.75	109.44	109.44	109.44	109.44	0	0	0	19.0264	19.575	-0.00141
$ZC_1C_2C_3$	2.09711	2.09711	3.4252	-15.75493	-15.75493	0.86359	0.86359	1	1	0.75	109.44	109.44	109.44	109.44	0	0	0	31.7694	31.762	0.00005
$ZC_1C_2C_3C_4$	2.91547	2.91547	4.7958	-16.68412	-16.68412	0.81549	0.81549	1	0.6965	0.75	109.44	109.44	109.44	109.44	-1.85936	0	0	43.91804	43.933	0.00035
$ZC_1C_2C_3C_4C_5$	2.91547	2.91547	4.1633	-15.50033	-14.82575	0.87495	0.87495	1	0.75	0.75	110.67	110.67	110.67	110.67	0	0	0	56.0274	56.089	0.00024
$ZC_1C_2C_3C_4C_5C_6$	2.91547	2.91547	4.1633	-15.50033	-14.82575	0.87495	0.87495	1	0.75	0.75	110.67	110.67	110.67	110.67	0	0	0	68.14830	68.181	0.00009
$ZC_1C_2C_3C_4C_5C_6C_7$	2.91547	2.91547	4.1633	-15.50033	-14.82575	0.87495	0.87495	1	0.75	0.75	110.67	110.67	110.67	110.67	0	0	0	80.39114	80.461	0.00094
$ZC_1C_2C_3C_4C_5C_6C_7C_8$	2.91547	2.91547	4.1633	-15.50033	-14.82575	0.87495	0.87495	1	0.75	0.75	110.67	110.67	110.67	110.67	0	0	0	92.54884	92.570	0.00025
$ZC_1C_2C_3C_4C_5C_6C_7C_8C_9$	2.91547	2.91547	4.1633	-15.50033	-14.82575	0.87495	0.87495	1	0.75	0.75	110.67	110.67	110.67	110.67	0	0	0	104.70000	104.700	0.00000
$ZC_1C_2C_3C_4C_5C_6C_7C_8C_9C_{10}$	2.91547	2.91547	4.1633	-15.50033	-14.82575	0.87495	0.87495	1	0.75	0.75	110.67	110.67	110.67	110.67	0	0	0	116.83344	116.834	-0.00004
$ZC_1C_2C_3C_4C_5C_6C_7C_8C_9C_{10}C_{11}$	2.91547	2.91547	4.1633	-15.50033	-14.82575	0.87495	0.87495	1	0.75	0.75	110.67	110.67	110.67	110.67	0	0	0	128.96677	128.967	-0.00002



SULFIDES ( $C_nH_{2n+2}S_m$ ,  $n = 2, 3, 4, 5, \dots, \infty$ )

The alkyl sulfides,  $C_nH_{2n+2}S_m$ , comprise two types of  $C-S$  functional groups, one for t-butyl groups corresponding to the  $C$  and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl  
 10 ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each  $C-S$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO  
 15 and the  $S$  AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243),  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. As in the case of thiols,  $C_2$  of Eq. (15.52) for the  $C-S$ -bond MO given by Eq. (15.127) is  $C_2(C2sp^3HO \text{ to } S) = 0.64965$ .

20 The  $C-S$  group of alkyl sulfides is equivalent to that of thiols where  $E_r(atom-atom, msp^3.AO)$  is  $-0.72457 \text{ eV}$  (Eq. (14.151)). The t-butyl- $C-S$  group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table  
 25 15.153. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the  $C-S$  bond is along the  $x$  axis in the  $xy$ -plane. The  $S$  nucleus is at the focus  $+c$  and the  $C$  nucleus is at the focus  $-c$ . The elliptic angle  $\theta'$  is taken as counterclockwise from the  $x$ -axis for  $S$  and as clockwise from the  $-x$ -axis  
 30 for  $C$ . The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum



over the integer multiple of each  $E_D(\text{Group})$  of Table 15.156 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.79-15.108) are given in Table 15.158.



Table 15.153. The symbols of functional groups of alkyl sulfides.

Functional Group	Group Symbol
C-S (methyl, alkyl)	C-S (f)
C-S ((CH <sub>3</sub> ), C-S-)	C-S (fi)
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C-C' (a)
CC bond (iso-C)	C-C' (b)
CC bond (tert-C)	C-C' (c)
CC (iso to iso-C)	C-C' (d)
CC (t to t-C)	C-C' (e)
CC (t to iso-C)	C-C' (f)

Table 15.154. The geometrical bond parameters of alkyl sulfides and experimental values [1].

Parameter	C-S (f) Group	C-S (fi) Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C' (a) Group	C-C' (b) Group	C-C' (c) Group	C-C' (d) Group	C-C' (e) Group	C-C' (f) Group
<i>a</i> (Å)	1.90975	1.90975	1.04920	1.07122	1.07465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
<i>c'</i> (Å)	1.71455	1.71455	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length	1.81460	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
2 <i>c'</i> (Å)											
Exp. Bond Length (Å)	1.807 (dimethyl sulfide)	1.807 (dimethyl sulfide)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
	1.813 (ethyl methyl sulfide, avg.)	1.813 (ethyl methyl sulfide, avg.)	1.117 (C-H butane)	1.117 (C-H butane)		1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)
<i>t<sub>sc</sub></i> (Å)	0.84112	0.84112	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
<i>ε</i>	0.89778	0.89778	0.63380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.155. The MO to HO intercept geometrical bond parameters of alkyl sulfides.  $R, R', R'',$  are H or alkyl groups.  $E_f$  is  $E_f(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Bond	Atom	$E_f$ (eV) Bond 1	$E_f$ (eV) Bond 2	$E_f$ (eV) Bond 3	$E_f$ (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{\text{bond}}$ ( $a_0$ )	$r_{\text{bond}}$ ( $a_0$ )	$E_f$ (eV) Final	$E(C2sp^3)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$R-S-R$ ( $C-S$ (i) and (ii))	S	-0.36229	-0.36229	0	0		1.32010	0.87495	-15.55033		129.96	50.04	52.88	1.15262	0.56193
$H_3C-S-C_6H_5CH_2R$ ( $C-S$ (i))	C	-0.36229	0	0	0	-151.97798	0.91771	0.89382	-15.18804	-14.99117	130.79	49.21	53.75	1.10937	0.58518
$H_3C-S-C_6H_5CH_2R$ ( $C-S$ (ii))	C	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
$H_3C-S-C_6H_5CH_2R$ ( $C-S$ (i) and (ii))	C	-0.36229	-0.72457	-0.72457	-0.72457	-154.15170	0.91771	0.78367	-17.36176	-17.17090	125.97	54.03	48.94	1.25430	0.46025
$C-H$ ( $CH_3$ )	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ ( $CH_2$ )	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ ( $CH$ )	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C-S-C_6H_5CH_2-$ ( $C-C$ (a))	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C-S-C_6H_5CH_2-$ ( $C-C$ (b))	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_3C-S-C_6H_5CH_2-$ ( $C-C$ (c))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_3C-S-C_6H_5CH_2-$ ( $C-C$ (d))	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50370
$R-H_3C-S-C_6H_5CH_2-$ ( $C-C$ (e))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61530	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_3C-S-C_6H_5CH_2-$ ( $C-C$ (f))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$R-H_3C-S-C_6H_5CH_2-$ ( $C-C$ (g))	C	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92445	0.47279
$R-H_3C-S-C_6H_5CH_2-$ ( $C-C$ (h))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.156. The energy parameters (eV) of functional groups of alkyl sulfides.

Parameters	C-S (i) Group	C-S (ii) Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0
$\zeta_1$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_2$	0.64965	0.64965	1	1	1	1	1	1	1	1	1
$\zeta_3$	1	1	1	1	1	1	1	1	1	1	1
$\zeta_4$	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\zeta_5$	0	0	0	1	1	0	0	0	1	1	0
$\zeta_6$	2	2	1	1	1	2	2	2	2	2	2
$\zeta_7$	0	0	3	2	1	0	0	0	0	0	0
$\zeta_8$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_9$	0.64965	0.64965	1	1	1	1	1	1	1	1	1
$\zeta_{10}$	-46.36495	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$\zeta_{11}$	7.93551	7.93551	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$\zeta_{12}$	12.13899	12.13899	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$\zeta_{13}$	-6.06949	-6.06949	-16.26937	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$\zeta_{14}$	0	0	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{H_{10}}(eV)$	-0.72457	-0.72457	0	0	0	0	0	0	0	0	0
$E_1(eV)$	0.72457	0.72457	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_2(eV)$	-31.63537	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63533	-31.63537	-31.63533	-31.63533
$E_3(eV)$	-0.72457	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_4(eV)$	-32.35994	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega(10^{15} rad/s)$	30.5436	8.92777	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	15.4846	9.55643
$E_5(eV)$	20.10434	5.87641	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_6(eV)$	-0.28705	-0.15519	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{K_{10}}(eV)$	0.08146	0.08146	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{K_{11}}(eV)$	-0.24632	-0.11446	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{K_{12}}(eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{K_{13}}(eV)$	-32.60626	-32.47440	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{K_{14}}(eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{K_{15}}(eV)$	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{K_{16}}(eV)$	3.33648	3.20462	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734



Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{D(mag)} (eV)$  values based on composition is given by (15.58).

Formula	Name	C-S (i) Group	C-S (ii) Group	CH <sub>3</sub>	CH <sub>2</sub>	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	$E_{mag}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> S	Dimethyl sulfide	2	0	2	0	0	0	0	0	0	0	0	0	31.6568	31.672	0.00048
C <sub>3</sub> H <sub>8</sub> S	Ethyl methyl sulfide	1	0	2	1	0	0	0	0	0	0	0	0	43.8138	43.848	0.00078
C <sub>4</sub> H <sub>10</sub> S	Diethyl sulfide	2	0	2	2	0	0	0	0	0	0	0	0	55.97208	56.043	0.00126
C <sub>5</sub> H <sub>12</sub> S	Methyl propyl sulfide	2	0	2	2	0	0	0	0	0	0	0	0	55.97208	56.029	0.00102
C <sub>6</sub> H <sub>14</sub> S	Isopropyl methyl sulfide	2	0	3	0	1	0	2	0	0	0	0	0	56.07297	56.115	0.00075
C <sub>7</sub> H <sub>16</sub> S	Butyl methyl sulfide	2	0	2	3	0	3	0	0	0	0	0	0	68.12978	68.185	0.00081
C <sub>8</sub> H <sub>18</sub> S	t-Butyl methyl sulfide	1	1	4	0	0	0	0	3	0	0	0	-1	68.28245	68.381	0.00144
C <sub>9</sub> H <sub>20</sub> S	Ethyl propyl sulfide	1	0	2	3	0	3	0	0	0	0	0	0	68.12978	68.210	0.00117
C <sub>10</sub> H <sub>22</sub> S	Diisopropyl sulfide	2	0	3	2	1	1	0	0	0	0	0	0	68.23067	68.350	0.00174
C <sub>11</sub> H <sub>24</sub> S	Butyl ethyl sulfide	2	0	2	4	0	4	0	0	0	0	0	0	80.48926	80.542	0.00065
C <sub>12</sub> H <sub>26</sub> S	Methyl pentyl sulfide	2	0	2	4	0	4	0	0	0	0	0	0	80.28748	80.395	0.00133
C <sub>13</sub> H <sub>28</sub> S	Diethyl sulfide	2	0	2	6	0	6	0	0	0	0	0	0	80.28748	80.332	0.00056
C <sub>14</sub> H <sub>30</sub> S	Di-sec-butyl sulfide	2	0	2	4	2	2	4	0	0	0	0	0	104.60288	104.701	0.00094
C <sub>15</sub> H <sub>32</sub> S	Di-t-butyl sulfide	2	0	6	0	0	0	0	6	0	0	0	0	104.80466	104.701	-0.00099
C <sub>16</sub> H <sub>34</sub> S	Diisobutyl sulfide	2	0	4	2	2	0	6	0	0	0	0	-2	104.90822	104.920	0.00011
C <sub>17</sub> H <sub>36</sub> S	Dipentyl sulfide	2	0	2	8	0	8	0	0	0	0	0	0	104.74800	104.834	0.00082
C <sub>18</sub> H <sub>38</sub> S	Diisopentyl sulfide	2	0	4	4	2	2	6	0	0	0	0	0	128.91828	128.979	0.00047
C <sub>19</sub> H <sub>40</sub> S		2	0	4	4	2	2	6	0	0	0	0	0	129.06340	129.151	0.00068



Table 15.158. The bond angle parameters of alkyl sulfides and experimental values [1]. In the calculation of  $\theta_2$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(atom-atom, msp, AO)$ .

Atoms of Angle	$2c_1'$ Bond 1 ( $\theta_0$ )	$2c_2'$ Bond 2 ( $\theta_0$ )	$2c_3'$ Terminal Atoms ( $\theta_0$ )	$E_{\text{terminal}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3 A)	$E_{\text{central}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3 A)	$c_2$ Atom 1	$c_1$ Atom 2	$C_1$	$C_2$	$c_1'$	$c_2'$	$E_r$ (eV)	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C_a S C_a$ (C-S-C (II))	3.42910	3.42910	5.2173	-16.11722	11	-16.11722	11	0.84418	0.84418	1	1	1	0.84418	-1.83836			99.06	99.05 (dimethyl sulfide)
$\angle C_a S C_b$ (C-S-C (I))	3.42910	3.42910	5.1381	-15.75493 methyl $C_a$	7	-16.68412	25	0.86359	0.81549	1	1	1	0.83954	-1.83836			97.04	97 (ethyl methyl sulfide)
$\angle S C_a C_b$ (C-S-C (II))	3.42910	2.91547	5.3364	-10.36001	S	-16.27490	15	0.64965 (Eq. (15.127))	0.83600	1	0.64965 (Eq. (15.127))	1	0.74282	-0.72457			114.27	114.0 (ethyl methyl sulfide)
Methyl $\angle H C_a H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0			108.44	107 (propane)
$\angle C_a C_b C_c$															69.51		110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_a C_b H$															69.51		110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle H C_a C_b$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0			109.50	109.3 (dimethyl sulfide) 110 (ethyl methyl sulfide)
$\angle C_a C_b C_c$															70.56		109.44	
$\angle C_a C_b H$															70.56		109.44	
$\angle C_b C_a C_c$	2.91547	2.91547	4.7958	-16.68412	25	-16.68412	25	0.81549	0.81549	1	1	1	0.81549	-1.83836			110.57	110.8 (isobutane)
$\angle C_b C_a H$	2.91547	2.11323	4.1633	-15.55033	S	-14.82575	1	0.87495	0.91771	0.75	1	0.75	1.04887	0			110.76	
$\angle C_b C_a C_c$	2.91547	2.91547	4.1633	-15.55033	S	-14.82575	1	0.87495	0.91771	0.75	1	0.75	1.04887	0			111.27	111.4 (isobutane)
$\angle C_b C_a H$	2.90327	2.90327	4.7958	-15.55033	S	-14.82575	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.83836			111.27	111.4 (isobutane)
$\angle C_b C_a C_c$															72.50		107.50	



# DISULFIDES ( $C_nH_{2n+2}S_{2m}$ , $n = 2, 3, 4, 5, \dots, \infty$ )

The alkyl disulfides,  $C_nH_{2n+2}S_{2m}$ , comprise  $C-S$  and  $S-S$  functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise 10 functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each  $C-S$  group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulfides,  $C_2$  of Eq. (15.52) for the  $C-S$  bond MO given by Eq. (15.127) is  $C_2(C2sp^3HO \text{ to } S) = 0.64965$  and 15  $E_T(atom - atom, msp^3.AO)$  is  $-0.72457 \text{ eV}$  (Eq. (14.151)).

The  $S-S$  group is solved as an  $H_2$ -type-ellipsoidal-MO that is energy matched to the energy of sulfur,  $E(S) = -10.36001 \text{ eV}$ , such that  $E(AO / HO) = -10.36001 \text{ eV}$  in Eq. (15.42) with  $E_T(AO / HO) = E(AO / HO)$ . The  $S-S$ -bond MO is further energy matched to the  $C2sp^3$  HO of the  $C-S$ -bond MO.  $C_2$  of Eq. (15.52) for the  $S-S$ -bond MO given by Eq. 20 (15.127) is also  $C_2(C2sp^3HO \text{ to } S) = 0.64965$ . In order to match  $E_T(atom - atom, msp^3.AO)$  of the  $C-S$  group ( $-0.72457 \text{ eV}$  (Eq. (14.151))),  $E_T(atom - atom, msp^3.AO)$  of the  $S-S$ -bond MO is determined using a linear combination of the AOs corresponding to  $-0.72457 \text{ eV}$  and  $0 \text{ eV}$  in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is  $E_T(atom - atom, msp^3.AO) = -0.36229 \text{ eV}$ .

25 The symbols of the functional groups of branched-chain alkyl disulfides are given in Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given



in Table 15.163 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.162 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.79-15.108) are given in Table 15.164.



Table 15.159. The symbols of functional groups of alkyl disulfides.

Functional Group	Group Symbol
C-S	C-S
S-S	S-S
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.160. The geometrical bond parameters of alkyl disulfides and experimental values [1].

Parameter	C-S (f) Group	S-S Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a$ (Å)	1.90975	2.37173	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.71455	1.91070	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.81460	2.02220	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.816 (dimethyl disulfide)	2.029 (dimethyl disulfide)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c$ (Å)	0.84112	1.40510	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.89778	0.80562	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.161. The MO to HO intercept geometrical bond parameters of alkyl disulfides.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(Atom - atom, msp, AO)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy ( $C_{2sp}^*$ , eV)	$r_{final}$ ( $a_0$ )	$E_{rindorb}$ (eV) Final	$E(C_{2sp}^*)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
RS-SR (C-S (i) and (ii))	S	-0.36229	-0.18114	0	0		1.32010	-15.36918		94.25	85.75	38.93	1.84513	0.06558
$H_3C_a-SS-C_aH_2CH_2R$	C <sub>a</sub>	-0.36229	0	0	0	-151.97798	0.91771	-15.18804	-14.99717	130.79	49.21	53.75	1.12937	0.58518
$H_3C_a-SS-C_aH_2CH_2R$ (C-S (i))	C <sub>a</sub>	-0.36229	-0.92918	0	0	-152.90716	0.91771	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
C-H (CH <sub>3</sub> )	C <sub>e</sub>	-0.36229	-0.72457	-0.72457	-0.72457	-154.15170	0.91771	-17.36176	-17.17090	125.97	54.03	48.94	1.25430	0.46025
C-H (CH <sub>2</sub> )	C <sub>i</sub>	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	-15.56407	77.49	102.51	41.48	1.25564	0.18708
C-H (CH <sub>2</sub> )	C <sub>i</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.20933
C-H (CH)	C <sub>i</sub>	-0.92918	-0.92918	-0.92918	0	-154.40524	0.91771	-17.61330	-17.42244	61.10	118.90	31.57	1.42988	0.37326
$H_3C_aC_aH_2CH_2-$ (C-C (ii))	C <sub>a</sub>	-0.92918	0	0	0	-152.54487	0.91771	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$R-H_2C_a(H_2C_a-R')HCCH_2-$ (C-C (ii))	C <sub>a</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_a(R'-H_2C_a)C_a(R''-H_2C_a)CH_2-$ (C-C (ii))	C <sub>a</sub>	-0.92918	-0.92918	-0.92918	0	-154.40524	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$isoC_aC_a(H_2C_a-R')HCCH_2-$ (C-C (ii))	C <sub>a</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	-17.92866	-17.73779	48.21	131.79	21.74	1.97354	0.50570
$tertC_a(R'-H_2C_a)C_a(R''-H_2C_a)CH_2-$ (C-C (ii))	C <sub>a</sub>	-0.92918	-0.92918	-0.92918	0	-154.40524	0.91771	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(H_2C_a-R')HCCH_2-$ (C-C (ii))	C <sub>a</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.56	22.66	1.94462	0.49298
$tertC_a(H_2C_a-R')HCCH_2-$ (C-C (ii))	C <sub>a</sub>	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$tertC_a(R'-H_2C_a)C_a(R''-H_2C_a)CH_2-$ (C-C (ii))	C <sub>a</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	-17.92866	-17.73779	50.04	129.56	22.66	1.94462	0.49298



Table 15.162. The energy parameters (eV) of functional groups of alkyl disulfides.

Parameters	C-S (f)	S-S Group	C-H <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	C-C (f) Group
$\eta_1$	1	1	3	1	1	1	1	1	1	1	1
$\eta_2$	0	0	2	0	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0
$\zeta_1$	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_2$	0.64965	0.64965	1	1	1	1	1	1	1	1	1
$\zeta_3$	1	1	1	1	1	1	1	1	1	1	1
$\zeta_4$	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\zeta_5$	0	0	0	1	0	0	0	1	1	1	0
$\zeta_6$	2	2	1	1	2	2	2	2	2	2	2
$\zeta_7$	0	0	3	1	0	0	0	0	0	0	0
$\zeta_{10}$	0.5	0.5	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_{20}$	0.64965	0.64965	1	1	1	1	1	1	1	1	1
$V_e$ (eV)	-46.36495	-31.74215	-107.32728	-70.41425	-28.79214	-28.79214	-28.79214	-28.79214	-29.10112	-29.10112	-29.10112
$V_p$ (eV)	7.95551	7.12083	38.92728	25.78002	9.33552	9.33552	9.33552	9.33552	9.37273	9.37273	9.37273
$T$ (eV)	12.13899	6.69177	32.53914	21.06675	6.77464	6.77464	6.77464	6.77464	6.90500	6.90500	6.90500
$V_m$ (eV)	-6.06949	-3.34589	-16.24697	-10.53337	-3.38732	-3.38732	-3.38732	-3.38732	-3.45250	-3.45250	-3.45250
$E_{1/2}^{\text{red}}(eV)$	0	-10.36001	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta F_{H_{1/2}}(eV)$	-0.72457	0	0	0	0	0	0	0	0	0	0
$E_{1/2}^{\text{red}}(eV)$	0.72457	-10.36001	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{1/2}^{\text{ox}}(eV)$	-31.63537	-31.63544	-67.69451	-49.66493	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$E_{1/2}^{\text{ox}}(eV)$	-0.72457	-0.36229	0	0	-1.85836	-1.85836	-1.44915	-1.44915	-1.44915	-1.44915	-1.44915
$E_{1/2}^{\text{ox}}(eV)$	-32.35994	-31.99766	-67.69450	-49.66493	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\omega$ (10 <sup>16</sup> rad/s)	30.5436	6.45076	24.9286	24.2751	9.43699	9.43699	9.43699	9.43699	9.55643	9.55643	9.55643
$E_k$ (eV)	20.10434	4.24600	16.40846	15.97831	6.21159	6.21159	6.21159	6.21159	6.29021	6.29021	6.29021
$E_p$ (eV)	-0.28705	-0.13044	-0.23552	-0.23017	-0.16515	-0.16515	-0.16515	-0.16515	-0.16416	-0.16416	-0.16416
$E_{\text{red}}$ (eV)	0.08146	0.06745	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
$E_{\text{red}}$ (eV)	-0.24652	-0.09672	-0.22757	-0.14502	-0.10359	-0.10359	-0.10359	-0.10359	-0.10260	-0.10260	-0.10260
$E_{\text{red}}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{1/2}^{\text{red}}$ (eV)	-32.60626	-32.09437	-67.92207	-49.80996	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$E_{\text{red}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{red}}$ (eV)	0	0	-13.59844	-13.59844	0	0	0	0	0	0	0
$E_{1/2}^{\text{red}}$ (eV)	3.35648	2.82459	12.49186	7.83016	4.32754	4.29921	4.29921	4.17951	3.97398	3.62128	3.91734

Table 15.163. The total bond energies of alkyl disulfides calculated using the functional group composition and the energies of Table 15.162 compared to the experimental values [3]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_{1/2}^{\text{red}}$  (eV) values based on composition is given by (15.58).

Formula	Name	C-S Group	S-S Group	C-H <sub>2</sub>	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	$E_{\text{mag}}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$\text{CH}_3\text{SS}_2$	Dimethyl disulfide	2	1	2	0	0	0	0	0	0	0	0	34.413	34.413	-0.00199
$\text{C}_2\text{H}_5\text{SS}_2$	Diethyl disulfide	2	1	2	0	2	0	0	0	0	0	0	58.79667	58.873	0.00120
$\text{C}_3\text{H}_7\text{SS}_2$	Diisopropyl disulfide	2	1	2	0	4	0	0	0	0	0	0	83.11207	83.169	0.00068
$\text{C}_4\text{H}_9\text{SS}_2$	Dibutyl disulfide	2	1	6	0	0	0	6	0	0	0	-2	107.99653	107.919	-0.00072



Table 15.164. The bond angle parameters of alkyl disulfides and experimental values [1]. In the calculation of  $\theta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

Atoms of angle	$2\phi_1$ Bond 1 ( $\phi_1$ )	$2\phi_2$ Bond 2 ( $\phi_2$ )	$2\phi_3$ Terminal Atoms ( $\phi_3$ )	$E_{\text{Calc}}^{\text{Calc}}$ Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{Calc}}^{\text{Calc}}$ Atom 2 Hybridization Designation (Table 15.3.A)	$c_1$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_3$	$E_r$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle \text{H-C-H}$	2.09711	2.09711	3.4232	-15.75403	H	0.86359	1	1	1	0.75	0	70.56			109.50	111.3 (dimethyl disulfide)
$\angle \text{S-C-H}$															109.44	111.3 (dimethyl disulfide)
$\angle \text{H-C-S}$	2.09711	3.42910	4.6230	-15.55033 $C_s$	S	0.87495	0.76144 (Eq. 15.126)	0.75	0.76144 (Eq. 15.126)	0.75	0				111.22	111.3 (dimethyl disulfide)
$\angle \text{S-C-S}$	3.82141	3.42910	5.7017	-10.36001 $S$	S	0.64965 (Eq. 15.127)	0.91771	1	0.64965 (Eq. 15.127)	1	-0.72457				102.57	103.2 (dimethyl disulfide)
Methyl $\angle \text{H-C-H}$	2.11106	2.11106	3.4232	-15.75403	H	0.86359	1	1	1	0.75	0				106.44	107 (propane)
$\angle \text{C-C-C}$																112 (propane)
$\angle \text{C-C-H}$																110.49 (butane)
Methyl $\angle \text{H-C-H}$	2.09711	2.09711	3.4232	-15.75403	H	0.86359	1	1	1	0.75	0				109.44	110.8 (isobutane)
$\angle \text{C-C-C}$																110.67 (isobutane)
$\angle \text{C-C-H}$	2.091547	2.091547	4.7958	-16.68412 $C_s$	2S	0.81549	0.81549	1	1	1	-1.83836				110.76	110.8 (isobutane)
$\angle \text{C-C-H}$	2.091547	2.11235	4.1633	-15.55033 $C_s$	1	0.87495	0.91771	0.75	1	0.75	0				111.27	111.4 (isobutane)
$\angle \text{C-C-H}$	2.091547	2.09711	4.1633	-15.55033 $C_s$	1	0.87495	0.91771	0.75	1	0.75	0				111.27	111.4 (isobutane)
$\angle \text{C-C-C}$	2.00327	2.00327	4.7958	-15.55033 $C_s$	1	0.87495	0.91771	0.75	1	0.75	-1.83836				107.50	



SULFOXIDES ( $C_nH_{2n+2}(SO)_m$ ,  $n = 2, 3, 4, 5 \dots \infty$ )

The alkyl sulfoxides,  $C_nH_{2n+2}(SO)_m$ , comprise a  $C-SO-C$  moiety that comprises  $C-S$  and  $SO$  functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The  $SO$  functional group comprises a double bond between the two unpaired electrons of  $O$ . The sulfur atom is energy matched to the  $C2sp^3$  HO. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $S$  AO has an initial energy of  $E(S) = -10.36001 \text{ eV}$  [38]. To meet the equipotential condition of the union of the  $S=O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $S=O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(S)} c_2(C2sp^3 HO) \\ &= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}} (0.91771) \\ &= 1.20632 \end{aligned} \quad (15.128)$$

The  $S$  atom also forms a single bond with each of the  $C2sp^3$  HOs of the two  $C-S$  groups. The formation of these bonds is permitted by the hybridization of the four electrons of the  $S3p$  shell to give the orbital arrangement:

$$\begin{array}{cccc} & \text{3sp}^3 \text{ state} & & \\ \uparrow & \uparrow & \uparrow & \uparrow \\ \hline 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \quad (15.129)$$



where the quantum numbers ( $\ell, m_\ell$ ) are below each electron. The  $3s$  shell remains unchanged. Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.118) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \text{ eV}$ . Using Eq. (15.16) with the radius of the sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the

5 outer electron of the  $S3sp^3$  shell is given by the sum of  $E_{Coulomb}(S3sp^3)$  and  $E(magnetic)$ :

$$\begin{aligned}
 E(S3sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{3sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_{16}^3} \\
 &= \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (1.32010a_0)^3} \\
 &= -11.57099 \text{ eV} + 0.04973 \\
 &= -11.52126 \text{ eV}
 \end{aligned} \tag{15.130}$$

Then, the hybridization energy  $E_{hybridization}(S3sp^3)$  of the  $S3sp^3$  HO is

$$\begin{aligned}
 E_{hybridization}(S3sp^3) &= E(S3sp^3) - E(S) \\
 &= -11.52126 \text{ eV} - 10.36001 \text{ eV} \\
 &= -1.16125 \text{ eV}
 \end{aligned} \tag{15.131}$$

The  $SO$  group is matched to the  $C-S$  group with which it shares the common

10 hybridized  $S$  atom. Consequently,  $E_{hybridization}(S3sp^3)$  is subtracted from  $E_r(Group)$  in the determination of  $E_D(Group)$  (Eq. 15.56)). Furthermore, the energy of the  $S=O$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized  $S$  atom such that

$$E(AO / HO) = E(S3sp^3) = -11.52126 \text{ eV} \quad \text{a n d}$$

$$15 \quad \Delta E_{H_2MO}(AO / HO) = E_{hybridization}(S3sp^3) = -1.16125 \text{ eV} . \quad \text{T h e n ,}$$

$E_r(AO / HO) = E(S) = -10.36001 \text{ eV}$ . Also,  $E_r(atom - atom, msp^3.AO)$  of the  $S=O$  bond is zero since there are no bonds with a  $C2sp^3$  HO.

The  $C-S$  group is solved as an energy minimum by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell and by hybridizing the four  $S3p$  electrons to form a

20  $S3sp^3$  shell, and the sharing of electrons between the  $C2sp^3$  HO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic



energy of the  $S3sp^3$  shell,  $E_{Coulomb}(S3sp^3)$  given by Eq. (15.120) in Eq. (15.63), the  $S3sp^3$ -shell hybridization factor,  $c_2(S3sp^3)$ , is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045 \quad (15.132)$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the  
 5 Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_1$  and  $c_2$   
 are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$   
 parameter. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq.  
 (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  
 $S3sp^3$  HO has an energy of  $E(S3sp^3) = -11.52126 \text{ eV}$  (Eq. (15.130)). To meet the  
 10 equipotential condition of the union of the  $C-S$   $H_2$ -type-ellipsoidal-MO with these orbitals,  
 the hybridization factor  $C_2$  of Eq. (15.52) for the  $C-S$ -bond MO given by Eqs. (15.68) and  
 (15.70) is

$$C_2(C2sp^3HO \text{ to } S3sp^3) = \frac{E(S3sp^3)}{E(C, 2sp^3)} c_2(S3sp^3) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}} (0.85045) = 0.66951 \quad (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of  $S$  matched to the  
 15 Coulombic energy between the electron and proton of  $H$ , the energy of the  $C-S$ -bond MO is  
 the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with

$$E(AO/HO) = 0 \quad \text{and} \quad E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO). \quad \text{For sulfoxides,}$$

$$\Delta E_{H_2MO}(AO/HO) = -0.72457 \text{ eV}. \quad \text{Further equivalently,}$$

$$E_T(atom - atom, msp^3.AO) = -0.72457 \text{ eV} \quad (\text{Eq. (14.151)}).$$

20 The symbols of the functional groups of branched-chain alkyl sulfoxides are given in  
 Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)),  
 and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in  
 Tables 15.166, 15.167, and 15.168, respectively. Consider that the  $C-S$  bond is along the  $x$   
 axis in the  $xy$ -plane. The  $S$  nucleus is at the focus  $+c$  and the  $C$  nucleus is at the focus  $-c$ . The  
 25 elliptic angle  $\theta'$  is taken as counterclockwise from the  $x$ -axis for  $S$  and as clockwise from the  
 $-x$ -axis for  $C$ . The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as  
 the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.168 corresponding to functional-



group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	$C-S$
SO	$SO$
CH <sub>3</sub> group	$C-H (CH_3)$
CH <sub>2</sub> group	$C-H (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C (a)$
CC bond (iso-C)	$C-C (b)$
CC bond (tert-C)	$C-C (c)$
CC (iso to iso-C)	$C-C (d)$
CC (t to t-C)	$C-C (e)$
CC (t to iso-C)	$C-C (f)$



Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

Parameter	C-S Group	SO Group	C'-H (CH <sub>3</sub> ) Group	C'-H (CH <sub>2</sub> ) Group	C-H Group	C'-C' (a) Group	C'-C' (b) Group	C-C' (c) Group	C-C' (d) Group	C-C' (e) Group	C-C' (f) Group
$\alpha$ (a)	1.87325	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (a)	1.67271	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length											
$2c'$ (A)	1.77031	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length	1.799 (dimethyl sulfoxide)	1.485 (dimethyl sulfoxide)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
			1.117 (C-H butane)	1.117 (C-H butane)		1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)	1.531 (butane)
$h, c'$ (a)	0.84328	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$\sigma$	0.89294	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides.  $E_r$  is  $E_r$  (atom - atom, msp, AO).

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy C2sp <sup>3</sup> (eV)	$r_{\text{final}}$ (a)	$r_{\text{final}}$ (a)	$E_{\text{orbital}}$ (eV) Final	$E$ (C2sp <sup>3</sup> ) (eV) Final	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a)	$d_2$ (a)
$R_2S=O$	S	0	-0.36229	-0.36229	0	-132010	0.87495	0.87495	-15.55033	-15.55033	79.78	38.00	1.56425	0.15529
$R_2S=O$	O	0	0	0	0	1.00000	0.91771	0.91771	-14.82575	-14.82575	84.06	40.75	1.50400	0.09504
$R-SO$	S	-0.36229	-0.36229	0	0	1.32010	0.87495	0.87495	-15.55033	-15.55033	129.35	53.36	1.11799	0.55472
$H_3C-SO-O-C_2H_5CH_2R$	C <sub>α</sub>	-0.36229	0	0	0	-151.97798	0.89382	0.89382	-15.18804	-15.18804	130.19	54.24	1.09461	0.57809
$H_3C-SO-O-C_2H_5CH_2R$	C <sub>β</sub>	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.05	52.03	1.15245	0.52026
$C-H$ (CH <sub>3</sub> )	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	41.48	1.23564	0.18708
$C-H$ (CH <sub>2</sub> )	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	35.84	1.55486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	31.37	1.42988	0.37226
$H_3C-C_2H_5CH_2CH_2-$ (C-C (a))	C <sub>α</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	30.08	1.83879	0.38106
$H_3C-C_2H_5CH_2CH_2-$ (C-C (b))	C <sub>β</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	26.06	1.90890	0.45117
$R-H_3C-C_2H_5CH_2CH_2-$ (C-C (c))	C <sub>α</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	21.90	1.97162	0.51388
$R-H_3C-C_2H_5CH_2CH_2-$ (C-C (d))	C <sub>β</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	21.74	1.95734	0.50570
$isoC_2H_5-C_2H_5CH_2CH_2-$ (C-C (e))	C <sub>α</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	21.90	1.97162	0.51388
$isoC_2H_5-C_2H_5CH_2CH_2-$ (C-C (f))	C <sub>β</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	22.66	1.94462	0.49298
$isoC_2H_5-C_2H_5CH_2CH_2-$ (C-C (g))	C <sub>α</sub>	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40669	-17.21783	52.78	24.04	1.93445	0.47279
$isoC_2H_5-C_2H_5CH_2CH_2-$ (C-C (h))	C <sub>β</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	22.66	1.94462	0.49298



Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfoxides.

Parameters	C-S Group	SO Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	2	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	0.66951	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1
$C_4$	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	0	1	1	0	0	0	1	1	0
$C_6$	2	4	1	1	1	2	2	2	2	2	2
$C_7$	0	1	3	2	1	0	0	0	0	0	0
$C_{10}$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{100}$	0.66951	1	1	1	1	1	1	1	1	1	1
$C_{1000}$	46.73032	82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_e$ (eV)	8.13401	19.31325	38.97728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$V_f$ (eV)	12.47306	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_g$ (eV)	-6.23653	-10.40592	-16.26937	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{100}$ (eV)	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{100,100}$ (eV)	-0.72457	-1.16125	0	0	0	0	0	0	0	0	0
$E_{100}$ (eV)	-0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{1000}$ (eV)	-31.63521	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{10000}$ (eV)	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{100000}$ (eV)	-32.35994	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ (10 <sup>10</sup> rad/s)	30.8880	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{100}$ (eV)	20.33104	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{1000}$ (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{10000}$ (eV)	0.08543	0.12832	0.35532	0.35532	0.35532	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
$E_{100000}$ (eV)	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{1000000}$ (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{10000000}$ (eV)	-32.60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{100000000}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{1000000000}$ (eV)	0	-1.16125	-15.59844	-15.59844	-13.59844	0	0	0	0	0	0
$E_{10000000000}$ (eV)	3.35611	3.68556	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula	Name	C-S Group	SO Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	CH Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>5</sub> SO	Dimethyl sulfoxide	2	1	2	0	0	0	0	0	0	0	0	33.52450	35.435	-0.00233
C <sub>3</sub> H <sub>7</sub> SO	Diethyl sulfoxide	2	1	2	2	0	2	0	0	0	0	0	59.83990	59.891	0.00085
C <sub>4</sub> H <sub>9</sub> SO	Dipropyl sulfoxide	2	1	2	4	0	4	0	0	0	0	0	84.15530	84.294	0.00165







SULFOXIDES ( $C_n H_{2n+2} (SO)_m$ ,  $n = 2, 3, 4, 5, \dots \infty$ )

The alkyl sulfoxides,  $C_n H_{2n+2} (SO)_m$ , comprise a  $C-SO-C$  moiety that comprises  $C-S$  and  $SO$  functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The  $SO$  functional group comprises a double bond between the two unpaired electrons of  $O$ . The sulfur atom is energy matched to the  $C2sp^3$  HO. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $S$  AO has an initial energy of  $E(S) = -10.36001 \text{ eV}$  [38]. To meet the equipotential condition of the union of the  $S=O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $S=O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(S)} c_2(C2sp^3 HO) \\ &= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}} (0.91771) \\ &= 1.20632 \end{aligned} \quad (15.128)$$

The  $S$  atom also forms a single bond with each of the  $C2sp^3$  HOs of the two  $C-S$  groups. The formation of these bonds is permitted by the hybridization of the four electrons of the  $S3p$  shell to give the orbital arrangement:

$$\begin{array}{cccc} & \text{3sp}^3 \text{ state} & & \\ 25 & \begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} & & (15.129) \end{array}$$



where the quantum numbers ( $\ell, m_\ell$ ) are below each electron. The  $3s$  shell remains unchanged. Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.118) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \text{ eV}$ . Using Eq. (15.16) with the radius of the sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the 5 outer electron of the  $S3sp^3$  shell is given by the sum of  $E_{Coulomb}(S3sp^3)$  and  $E(magnetic)$ :

$$\begin{aligned} E(S3sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{3sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_{16}^3} \\ &= \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (1.32010a_0)^3} \\ &= -11.57099 \text{ eV} + 0.04973 \\ &= -11.52126 \text{ eV} \end{aligned} \quad (15.130)$$

Then, the hybridization energy  $E_{hybridization}(S3sp^3)$  of the  $S3sp^3$  HO is

$$\begin{aligned} E_{hybridization}(S3sp^3) &= E(S3sp^3) - E(S) \\ &= -11.52126 \text{ eV} - 10.36001 \text{ eV} \\ &= -1.16125 \text{ eV} \end{aligned} \quad (15.131)$$

The  $SO$  group is matched to the  $C-S$  group with which it shares the common hybridized  $S$  atom. Consequently,  $E_{hybridization}(S3sp^3)$  is subtracted from  $E_r(Group)$  in the determination of  $E_D(Group)$  (Eq. 15.56). Furthermore, the energy of the  $S=O$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized  $S$  atom such that

$$E(AO / HO) = E(S3sp^3) = -11.52126 \text{ eV} \quad \text{a n d}$$

$$15 \quad \Delta E_{H_2MO}(AO / HO) = E_{hybridization}(S3sp^3) = -1.16125 \text{ eV} . \quad \text{T h e n ,}$$

$E_r(AO / HO) = E(S) = -10.36001 \text{ eV}$ . Also,  $E_r(atom - atom, msp^3.AO)$  of the  $S=O$  bond is zero since there are no bonds with a  $C2sp^3$  HO.

The  $C-S$  group is solved as an energy minimum by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell and by hybridizing the four  $S3p$  electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the  $C2sp^3$  HO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic



energy of the  $S3sp^3$  shell,  $E_{Coulomb}(S3sp^3)$  given by Eq. (15.120) in Eq. (15.63), the  $S3sp^3$ -shell hybridization factor,  $c_2(S3sp^3)$ , is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045 \quad (15.132)$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the  
5 Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  parameter. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $S3sp^3$  HO has an energy of  $E(S3sp^3) = -11.52126 \text{ eV}$  (Eq. (15.130)). To meet the  
10 equipotential condition of the union of the  $C-S$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the  $C-S$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3 HO \text{ to } S3sp^3) = \frac{E(S3sp^3)}{E(C, 2sp^3)} c_2(S3sp^3) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}} (0.85045) = 0.66951 \quad (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of  $S$  matched to the  
15 Coulombic energy between the electron and proton of  $H$ , the energy of the  $C-S$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with

$$E(AO/HO) = 0 \quad \text{and} \quad E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO). \quad \text{For sulfoxides,}$$

$$\Delta E_{H_2MO}(AO/HO) = -0.72457 \text{ eV}. \quad \text{Further equivalently,}$$

$$E_T(atom - atom, msp^3 AO) = -0.72457 \text{ eV} \quad (\text{Eq. (14.151)}).$$

20 The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the  $C-S$  bond is along the  $x$  axis in the  $xy$ -plane. The  $S$  nucleus is at the focus  $+c$  and the  $C$  nucleus is at the focus  $-c$ . The  
25 elliptic angle  $\theta'$  is taken as counterclockwise from the  $x$ -axis for  $S$  and as clockwise from the  $-x$ -axis for  $C$ . The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.168 corresponding to functional-



group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	$C-S$
SO	$SO$
CH <sub>3</sub> group	$C-H (CH_3)$
CH <sub>2</sub> group	$C-H (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C (a)$
CC bond (iso-C)	$C-C (b)$
CC bond (tert-C)	$C-C (c)$
CC (iso to iso-C)	$C-C (d)$
CC (t to t-C)	$C-C (e)$
CC (t to iso-C)	$C-C (f)$



Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

Parameter	C-S Group	S-O Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\alpha$ (°)	1.87325	1.98517	1.64920	1.67122	1.67465	2.12499	2.10725	2.12499	2.10725	2.10725
$\epsilon'$ (°)	1.67271	1.40896	1.04856	1.05553	1.05661	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (Å)	1.77031	1.49118	1.10974	1.11713	1.11827	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.799 (dimethyl sulfoxide)	1.485 (dimethyl sulfoxide)	1.107 (C-H propane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
$h, c$ (°)	0.84328	1.39847	1.27295	1.29569	1.29924	1.54616	1.52750	1.54616	1.52750	1.52750
$\epsilon$	0.89294	0.70974	0.63580	0.63159	0.63095	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	$i_T$ (eV) Bond 4	Final Total Energy C2sp <sup>2</sup> (eV)	$r_{\text{final}}$ (a <sub>0</sub> )	$r_{\text{final}}$ (a <sub>0</sub> )	$E_{\text{calculated}}$ (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	$\theta'$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
$R_2S=O$	S	0	-0.36229	-0.36229	0	0	1.32010	0.87495	0.87495	-15.50033		79.78	100.22	38.00	1.56425	0.15529
$R_2S=O$	O	0	0	0	0	0	1.00000	0.91771	0.91771	-14.8275		84.06	95.94	40.75	1.50400	0.09504
$R_2S=O$	S	-0.36229	-0.36229	0	0	0	1.32010	0.87495	0.87495	-15.50033		129.35	50.65	53.36	1.11799	0.54472
$H_3C-S(O)-C_1H_2CH_2R$	C <sub>1</sub>	-0.36229	0	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.19	49.81	34.24	1.09461	0.37809
$H_3C-S(O)-C_1H_2CH_2R$	C <sub>2</sub>	-0.36229	-0.92918	0	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.05	51.95	52.03	1.15245	0.52026
C-H (CH <sub>3</sub> )	C	-0.92918	0	0	0	0	-152.54487	0.91771	0.86359	-15.75093	-15.56407	77.49	102.51	41.48	1.23564	0.18708
C-H (CH <sub>2</sub> )	C	-0.92918	-0.92918	0	0	0	-153.47406	0.91771	0.81549	-16.08412	-16.09325	68.47	111.55	35.84	1.53486	0.29933
C-H (CH)	C	-0.92918	-0.92918	-0.92918	0	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C-C_1H_2CH_2CH_2CH_2R$	C <sub>1</sub>	-0.92918	0	0	0	0	-152.54487	0.91771	0.86359	-15.75093	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C-C_1H_2CH_2CH_2CH_2R$	C <sub>2</sub>	-0.92918	-0.92918	0	0	0	-153.47406	0.91771	0.81549	-16.08412	-16.09325	56.41	125.59	26.06	1.90890	0.45117
$R-H_2C-C_1H_2CH_2CH_2CH_2R$	C <sub>1</sub>	-0.92918	-0.92918	-0.92918	0	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C-C_1H_2CH_2CH_2CH_2R$	C <sub>2</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-0.72457	-154.71660	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_1H_2CH_2CH_2CH_2CH_2R$	C <sub>1</sub>	-0.92918	-0.92918	-0.92918	0	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$isoC_1H_2CH_2CH_2CH_2CH_2R$	C <sub>2</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-0.72457	-154.71660	0.91771	0.75889	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$isoC_1H_2CH_2CH_2CH_2CH_2R$	C <sub>3</sub>	-0.92918	-0.92918	-0.92918	0	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	52.78	127.22	24.04	1.92443	0.47279
$isoC_1H_2CH_2CH_2CH_2CH_2R$	C <sub>4</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-0.72457	-154.71660	0.91771	0.75889	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfoxides.

Parameters	C-S Group	SO Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	1	2	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	0.66951	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1
$C_4$	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	0	1	1	0	0	0	1	1	0
$C_6$	2	4	1	1	1	2	2	2	2	2	2
$C_7$	0	1	3	2	1	0	0	0	0	0	0
$C_{10}$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{10}$	0.66951	1	1	1	1	1	1	1	1	1	1
$V_1$ (eV)	-46.73032	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_2$ (eV)	8.13401	19.31325	38.92728	25.78002	12.87680	9.33532	9.33532	9.37273	9.33532	9.37273	9.37273
$T$ (eV)	12.47306	20.81183	32.55914	21.06675	10.48382	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_3$ (eV)	-6.23653	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{10}$ (eV)	0	-11.32126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{10}$ (eV)	-0.72457	-1.16125	0	0	0	0	0	0	0	0	0
$E_{10}$ (eV)	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{10}$ (eV)	-31.63551	-63.27088	-67.69451	-49.66493	-31.63553	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{10}$ (eV)	-0.72457	0	0	0	0	0	0	0	0	0	0
$E_{10}$ (eV)	-32.35994	-63.27074	-67.69450	-49.66493	-31.63537	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$\omega$ (10 <sup>16</sup> rad/s)	30.8880	17.6762	24.9786	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{10}$ (eV)	20.33104	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{10}$ (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{10}$ (eV)	0.08543	0.12832	0.35532	0.35532	0.35532	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
$E_{10}$ (eV)	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{10}$ (eV)	0.14803	0.1441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{10}$ (eV)	-32.60589	-63.50937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{10}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{10}$ (eV)	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{10}$ (eV)	3.33611	3.86856	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula	Name	C-S Group	SO Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	CH Group	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>4</sub> SO	Dimethyl sulfoxide	2	1	2	0	0	0	0	0	0	0	0	33.52450	33.433	-0.00033
C <sub>2</sub> H <sub>6</sub> SO	Diethyl sulfoxide	2	1	2	2	0	0	0	0	0	0	0	59.85990	59.891	0.00085
C <sub>4</sub> H <sub>10</sub> SO	Diisopropyl sulfoxide	2	1	2	4	0	0	0	0	0	0	0	84.15550	84.294	0.00165



Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{AO})$ .

Atoms of angle	$2c_1'$ Bond 1 ( $\theta_1$ )	$2c_2'$ Bond 2 ( $\theta_2$ )	$2c_3'$ Terminal Atom ( $\theta_3$ )	$E_{\text{valence}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3 A)	$E_{\text{valence}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3 A)	$c_2$ Atom 1	$c_2$ Atom 2 (Eq. 15.114)	$C_1$	$C_2$	$C_3$	$\zeta_1$	$\zeta_2$	$E_T$ (eV)	$\theta_i$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C_1' C_2' C_3'$	3.34541	3.34541	4.9600	-16.47951	21	-16.47951	21	0.82562	0.82562	1	1	1	1	0.82562	-1.85836				96.20	96.6 (dimethyl sulfoxide)
$\angle C_1' S O$	3.34541	2.81792	4.9598	-15.18004	2	-15.18004	O	0.83395	0.83395 (Eq. 15.114)	1	1	1	1	0.87489	-1.65376				106.88	106.7 (dimethyl sulfoxide)
Methylene $\angle H C_1' H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_1' C_2' C_3'$																			110.49	112 (propane) 113.8 (isobutane) 110.8 (isobutane) 111.0 (isobutane) 111.4 (isobutane) 110.3 (dimethyl sulfoxide)
Methyl $\angle H C_1' H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	1	0.75	1.15796	0				109.50	109.44 109.44
$\angle C_1' C_2' C_3'$																			110.67	110.8 (isobutane)
$\angle C_1' C_2' C_3'$ iso $C_3'$	2.91547	2.91547	4.7958	-16.60412	25	$C_3'$	$C_3'$	0.81549	0.81549	1	1	1	1	0.81549	-1.85836				110.76	
$\angle C_1' C_2' C_3'$ iso $C_3'$	2.91547	2.11323	4.1633	-15.53033	5	$C_3'$	$C_3'$	0.87495	0.91771	0.75	1	0.75	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_1' C_2' C_3'$ iso $C_3'$	2.91547	2.09711	4.1633	-15.53033	5	$C_3'$	$C_3'$	0.87495	0.91771	0.75	1	0.75	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_1' C_2' C_3'$ tert $C_3'$	2.90327	2.90327	4.7958	-15.53033	5	$C_3'$	$C_3'$	0.87495	0.91771	0.75	1	0.75	0.75	1.04887	-1.85836				107.50	107.50



## DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle  $\theta_{\angle S=O/CSC'}$  between the plane defined by the CSC MO comprising a linear combination of two  $S-C$ -bond MOs and a line defined by the  $S=O$ -bond MO where  $S$  is the central atom is calculated using the results given in Table 15.170 and Eqs. (15.105-15.108). The distance  $d_1$  along the bisector of  $\theta_{\angle CSC'}$  from  $S$  to the internuclear-distance line between  $C$  and  $C$ ,  $2c'_{C-C}$ , is given by

$$d_1 = 2c'_{S-C} \cos \frac{\theta_{\angle CSC'}}{2} = 4.9800a_0 \cos \frac{96.20^\circ}{2} = 2.23423a_0 \quad (15.134)$$

where  $2c'_{S-C}$  is the internuclear distance between  $S$  and  $C$ . The atoms  $C$ ,  $C$ , and  $O$  define the base of a pyramid. Then, the pyramidal angle  $\theta_{\angle COC'}$  can be solved from the internuclear distances between  $C$  and  $C$ ,  $2c'_{C-C}$ , and between  $C$  and  $O$ ,  $2c'_{C-O}$ , using the law of cosines (Eq. (15.106)):

$$\begin{aligned} \theta_{\angle COC'} &= \cos^{-1} \left( \frac{(2c'_{C-O})^2 + (2c'_{C-O})^2 - (2c'_{C-C})^2}{2(2c'_{C-O})(2c'_{C-O})} \right) \\ &= \cos^{-1} \left( \frac{(4.95984)^2 + (4.95984)^2 - (4.9800)^2}{2(4.95984)(4.95984)} \right) \\ &= 60.27^\circ \end{aligned} \quad (15.135)$$

Then, the distance  $d_2$  along the bisector of  $\theta_{\angle COC'}$  from  $O$  to the internuclear-distance line  $2c'_{C-C}$ , is given by

$$d_2 = 2c'_{C-O} \cos \frac{\theta_{\angle COC'}}{2} = 4.95984a_0 \cos \frac{60.27^\circ}{2} = 4.28952a_0 \quad (15.136)$$

The lengths  $d_1$ ,  $d_2$ , and  $2c'_{S=O}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between  $O$  and  $S$ ,  $2c'_{S=O}$ , is the dihedral angle  $\theta_{\angle S=O/CSC'}$  that can be solved using the law of cosines (Eq. (15.108)):

$$\begin{aligned} \theta_{\angle S=O/CSC'} &= \cos^{-1} \left( \frac{d_1^2 + (2c'_{S=O})^2 - d_2^2}{2d_1(2c'_{S=O})} \right) \\ &= \cos^{-1} \left( \frac{(2.23423)^2 + (2.81792)^2 - (4.28952)^2}{2(2.23423)(2.81792)} \right) \\ &= 115.74^\circ \end{aligned} \quad (15.137)$$



The experimental [1] dihedral angle  $\theta_{\angle S=O/CSC}$  is

$$\theta_{\angle S=O/CSC} = 115.5^\circ$$

(15.138)



SULFITES ( $C_nH_{2n+2}(SO_3)_m$ ,  $n=2,3,4,5,\dots\infty$ )

The alkyl sulfites,  $C_nH_{2n+2}(SO_3)_m$ , comprise a  $C-O-SO-O-C$  moiety that comprises two types  $C-O$  functional groups, one for methyl and one for alkyl, and  $O-S$  and  $SO$  functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The  $SO$  functional group is equivalent to that of sulfoxides with  $E_T(atom - atom, msp^3.AO) = 0$  as given in the Sulfoxides section. The methyl and alkyl  $C-O$  functional groups having  $E_T(atom - atom, msp^3.AO) = -1.44915 \text{ eV}$  and  $E_T(atom - atom, msp^3.AO) = -1.65376 \text{ eV}$ , respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The  $SO$  functional group comprises a double bond between the  $S$  atom and the two unpaired electrons of  $O$ . The  $S$  atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the  $O-S$  groups is between the sulfur atom and a  $O2p$  AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the  $S3p$  shell to give the orbital arrangement given by Eq. (15.129). Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.120) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \text{ eV}$ . Using Eq. (15.16) with the radius of the



sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by the sum of  $E_{Coulomb}(S3sp^3)$  and  $E(magnetic)$  is  $E(S3sp^3) = -11.52126 \text{ eV}$  (Eq. (15.130)).

Thus, the  $O-S$  group is solved as an energy minimum by hybridizing the four  $S3p$  5 electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the  $O2p$  AO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  10 parameter. Each  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $S$  HO has an energy of  $E(S3sp^3) = -11.52126 \text{ eV}$ . To meet the equipotential condition of the union of the  $O-S$   $H_2$ -type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a  $C2sp^3$  HO, the hybridization factor  $C_2$  of Eq. (15.52) for the  $O-S$ -bond MO given by Eqs. 15 (15.68) and (15.70) is

$$\begin{aligned} C_2(S3sp^3 \text{ to } O \text{ to } C2sp^3 HO) &= \frac{E(S,3sp^3)}{E(O,2p)} c_2(C2sp^3 HO) \\ &= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}} (0.91771) \\ &= 0.77641 \end{aligned} \quad (15.139)$$

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of  $S$  matched to the Coulombic energy between the electron and proton of  $H$ , the energy of the  $O-S$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in 20 Eq. (15.42) with  $E(AO/HO) = 0$  and  $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$ . For sulfites,  $\Delta E_{H_2MO}(AO/HO) = -0.92918 \text{ eV}$  and equivalently,  $E_T(atom-atom,msp^3.AO) = -0.92918 \text{ eV}$  (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.



The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 5 15.175 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.79-15.108) are given in Table 15.182.

Table 15.177. The symbols of functional groups of alkyl sulfites.

Functional Group	Group Symbol
C-O (methyl)	$C-O$ (i)
C-O (alkyl)	$C-O$ (ii)
O-SO <sub>2</sub>	$O-S$
SO	$SO$
CH <sub>3</sub> group	$C-H$ (CH <sub>3</sub> )
CH <sub>2</sub> group	$C-H$ (CH <sub>2</sub> )
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)



Table 15.178. The geometrical bond parameters of alkyl sulfites and experimental values [1].

Parameter	C-O (i) Group	C-O (ii) Group	O-S	SO	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a$ (Å)	1.80717	1.79473	1.70299	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.34431	1.33968	1.48102	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.42276	1.41785	1.56744	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)			1.574 (H <sub>2</sub> SO <sub>4</sub> )	1.485 (dimethyl sulfide)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c$ (Å)	1.20776	1.19429	0.84069	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.74388	0.74645	0.86966	0.70974	0.63380	0.63159	0.63093	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.179. The MO to HO intercept geometrical bond parameters of alkyl sulfates.  $R, R', R''$  are H or alkyl groups.  $E_p$  is  $E_p(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Bond	Atom	$E_p$ (eV) Bond 1	$E_p$ (eV) Bond 2	$E_p$ (eV) Bond 3	$E_p$ (eV) Bond 4	Final Total Energy C2sp <sup>2</sup> (eV)	$r_{\text{final}}$ (a <sub>0</sub> )	$r_{\text{initial}}$ (a <sub>0</sub> )	$E_{\text{orbital}}$ (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	$\theta^*$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
$(\text{RO})_2\text{S}=\text{O}_a$	S	0	-0.46459	-0.46459	0		1.32010	0.86359	-15.75493		78.56	101.44	37.25	1.58026	0.17130
$(\text{RO})_2\text{S}=\text{O}_a$	O <sub>a</sub>	0	0	0	0		1.00000	0.91771	-14.82375		84.06	95.94	40.75	1.50400	0.09304
$\text{CH}_3\text{O}_a-\text{S}(\text{O})\text{OR}^*$	S	-0.46459	-0.46459	0	0		1.32010	0.86359	-15.75493		126.68	53.32	55.47	0.96321	0.51381
$\text{CH}_3\text{O}_a-\text{S}(\text{O})\text{OR}^*$	O <sub>a</sub>	-0.46459	-0.72457	0	0		1.00000	0.84957	-16.01492		126.03	53.97	54.81	0.98133	0.49959
$\text{RC}(\text{H})\text{O}_a-\text{S}(\text{O})\text{OR}^*$	O <sub>a</sub>	-0.46459	-0.82688	0	0		1.00000	0.84418	-16.11722		125.77	54.23	54.56	0.98753	0.49499
$\text{H}_3\text{C}_a-\text{O}_a\text{S}(\text{O})\text{OR}^*$	O <sub>a</sub>	-0.72457	-0.46459	0	0		1.00000	0.84957	-16.01492		93.85	86.15	44.57	1.28731	0.05700
$\text{H}_3\text{C}_a-\text{O}_a\text{S}(\text{O})\text{OR}^*$	C <sub>a</sub>	-0.72457	0	0	0	-152.34036	0.91771	0.87495	-15.55033	-15.33946	95.98	84.02	46.10	1.25319	0.09112
$\text{RH}_2\text{C}_a-\text{O}_a\text{S}(\text{O})\text{OR}^*$	O <sub>a</sub>	-0.82688	-0.46459	0	0		1.00000	0.84418	-16.11722		94.50	85.50	44.80	1.27343	0.06624
$\text{RH}_2\text{C}_a-\text{O}_a\text{S}(\text{O})\text{OR}^*$	C <sub>a</sub>	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.38181	-16.39093	92.41	87.59	43.35	1.30512	0.03456
$\text{C}^*-H(\text{C}^*)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$\text{C}^*-H(\text{C}^*)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$\text{C}^*-H(\text{C}^*)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	61.10	118.90	31.37	1.42988	0.37236
$\text{H}_3\text{C}_a\text{H}_2\text{C}_a\text{H}_2-\text{C}^*(\text{C}^*)$	C <sub>a</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$\text{H}_3\text{C}_a\text{H}_2\text{C}_a\text{H}_2-\text{C}^*(\text{C}^*)$	C <sub>a</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$	C <sub>a</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	48.30	131.70	21.90	1.97162	0.51388
$\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$	C <sub>a</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.73889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$	C <sub>a</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42344	48.30	131.70	21.90	1.97162	0.51388
$\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$	C <sub>a</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$	C <sub>a</sub>	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.93443	0.47279
$\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$	C <sub>a</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.180. The energy parameters (eV) of functional groups of allyl sulfites.

Parameters	C-O (i)	C-O (ii)	O-S	SO	CH <sub>3</sub>	CH <sub>2</sub>	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
$\eta_1$	1	1	1	2	2	2	1	1	1	1	1	1	1
$\eta_2$	0	0	0	0	1	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0	0	0
$\zeta_1$	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_2$	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
$\zeta_3$	1	1	1	1	1	1	1	1	1	1	1	1	1
$\zeta_4$	0.85395	0.85395	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\zeta_5$	0	0	0	0	0	1	1	0	0	0	1	1	0
$\zeta_6$	2	2	2	4	1	1	1	2	2	2	2	2	2
$\zeta_7$	0	0	0	1	3	2	1	0	0	0	0	0	0
$\zeta_8$	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$\zeta_9$	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
$\zeta_{10}$	-33.15757	-33.47304	-48.93512	-82.65003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_1$ (eV)	10.12103	10.15605	9.18680	19.31325	38.92728	25.78002	12.87680	9.33552	9.33552	9.37273	9.33552	9.37273	9.37273
$T$ (eV)	9.17389	9.32537	14.36741	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_{\text{an}}$ (eV)	-4.58695	-4.66268	-7.18371	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{\text{an}}$ (eV)	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{\text{an}}$ (eV)	-1.4915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0	0	0	0
$E_{\text{r}}$ (eV)	-13.18574	-12.98113	0.92918	-10.56001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{\text{r}}$ (eV)	-31.63533	-31.63544	-31.63543	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{\text{r}}$ (eV)	-1.4915	-1.65376	-0.92918	0	0	0	0	-1.83836	-1.83836	-1.44915	-1.83836	-1.44915	-1.44915
$E_{\text{r}}$ (eV)	-33.08452	-33.28912	-32.56455	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ (10 <sup>15</sup> rad/s)	22.0240	12.1583	33.4164	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{\text{r}}$ (eV)	14.49660	8.00277	21.99527	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{\text{r}}$ (eV)	-0.24921	-0.18631	-0.30214	-0.21348	-0.25532	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{\text{r}}$ (eV)	0.13663	0.13663	0.08679	0.12832	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{\text{r}}$ (eV)	1211	1211	1421	1431	1431	1431	1431	1431	1431	1431	1431	1431	1431
$E_{\text{r}}$ (eV)	-0.18089	-0.11799	-0.22875	-0.14952	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{\text{r}}$ (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\text{r}}$ (eV)	-33.26541	-33.40711	-32.82530	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.26541	-33.59732	-33.18712	-33.18712
$E_{\text{r}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{r}}$ (eV)	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\text{r}}$ (eV)	3.99563	4.13733	3.55352	3.68556	12.49186	7.85016	3.36601	4.32754	4.29921	3.97598	4.17951	3.62128	3.91734

Table 15.181. The total bond energies of allyl sulfites calculated using the functional group composition and the energies of Table 15.180 compared to the experimental values [3].

Formula	C-O (i)	C-O (ii)	O-S	SO	CH <sub>3</sub>	CH <sub>2</sub>	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> SO <sub>2</sub>	2	0	2	1	2	0	0	0	0	0	0	0	0	43.95038	44.042	0.00207
CH <sub>3</sub> SO <sub>2</sub>	0	2	2	1	2	2	2	0	0	0	0	0	0	68.54939	68.648	0.00143
CH <sub>3</sub> SO <sub>2</sub>	0	2	2	1	2	6	6	0	0	0	0	0	0	117.18019	117.191	0.00069







# SULFATES ( $C_nH_{2n+2}(SO_4)_m$ , $n=2,3,4,5,\dots,\infty$ )

The alkyl sulfates,  $C_nH_{2n+2}(SO_4)_m$ , comprise a  $C-O-SO_2-O-C$  moiety that comprises two types  $C-O$  functional groups, one for methyl and one for alkyl, and  $O-S$  and  $SO_2$  functional groups. The alkyl portion of the alkyl sulfate may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl  $C-O$  functional groups having  $E_r(atom-atom,msp^3.AO)=-1.44915\text{ eV}$  and  $E_r(atom-atom,msp^3.AO)=-1.65376\text{ eV}$ , respectively, are equivalent to the corresponding groups given in the Sulfites section. The  $O-S$  functional group having  $E_r(atom-atom,msp^3.AO)=-0.92918\text{ eV}$  is equivalent to that given in the Sulfites section. The  $SO_2$  functional group is equivalent to that of sulfones with  $E_r(atom-atom,msp^3.AO)=0$  as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each  $E_p(group)$  of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.79-15.108) are given in Table 15.188.



Table 15.183. The symbols of functional groups of alkyl sulfates.

Functional Group	Group Symbol
C-O (methyl)	C-O (i)
C-O (alkyl)	C-O (ii)
O-SO <sub>3</sub>	O-S
SO <sub>3</sub>	SO <sub>3</sub>
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C-C' (a)
CC bond (iso-C)	C-C' (b)
CC bond (tert-C)	C-C' (c)
CC (iso to iso-C)	C-C' (d)
CC (t to t-C)	C-C' (e)
CC (t to iso-C)	C-C' (f)

Table 15.184. The geometrical bond parameters of alkyl sulfates and experimental values [1].

Parameter	C-O (i) Group	C-O (ii) Group	O-S	SO <sub>3</sub>	C-H (CH <sub>3</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a$ (Å)	1.80717	1.79473	1.70299	1.83851	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.34451	1.33968	1.48102	1.36327	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length	1.42276	1.41785	1.56744	1.44282	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
$2c'$ (Å)												
Exp. Bond Length (Å)			1.574 (H <sub>2</sub> SO <sub>4</sub> )	1.435 (dimethyl sulfone)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c'$ (Å)	1.20776	1.19429	0.84069	1.26315	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e'$	0.74388	0.74645	0.86966	0.73353	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl sulfates.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^2, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy C2,sp <sup>2</sup> (eV)	$r_{\text{final}}$ (a <sub>0</sub> )	$r_{\text{final}}$ (a <sub>0</sub> )	$E_{\text{Final}}$ (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	$\theta^*$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
$(\text{RO})_2(\text{O}_2)\text{S}=\text{O}_s$	S	0	0	-0.46459	-0.46459		1.32010	0.86359	-15.75493		90.46	89.54	43.13	1.35635	0.00693
$(\text{RO})_2(\text{O}_2)\text{S}=\text{O}_s$	O <sub>s</sub>	0	0	0	0		1.00000	0.91771	-14.82575		95.05	84.95	46.36	1.28256	0.08071
$\text{CH}_3\text{O}_2-\text{S}(\text{O}_2)\text{OR}^*$	S	-0.46459	-0.46459	0	0		1.32010	0.86359	-15.75493		126.68	53.32	55.47	0.96521	0.51581
$\text{CH}_3\text{O}_2-\text{S}(\text{O}_2)\text{OR}^*$	O <sub>s</sub>	-0.46459	-0.72457	0	0		1.00000	0.84957	-16.01492		126.03	53.97	54.81	0.98133	0.49569
$(\text{C}-\text{O}(\text{ii}))$	O <sub>s</sub>	-0.46459	-0.82688	0	0		1.00000	0.84418	-16.11722		125.77	54.23	54.56	0.98753	0.49349
$\text{RCH}_2\text{O}_2-\text{S}(\text{O}_2)\text{OR}^*$	O <sub>s</sub>	-0.46459	-0.82688	0	0		1.00000	0.84957	-16.01492		93.85	86.15	44.57	1.28731	0.05700
$\text{H}_3\text{C}_s-\text{O}_2\text{S}(\text{O}_2)\text{OR}$	O <sub>s</sub>	-0.72457	-0.46459	0	0		1.00000	0.84957	-16.01492		93.85	86.15	44.57	1.28731	0.05700
$\text{H}_3\text{C}_s-\text{O}_2\text{S}(\text{O}_2)\text{OR}$	C <sub>s</sub>	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.53033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$\text{RH}_2\text{C}_s-\text{O}_2\text{S}(\text{O}_2)\text{OR}^*$	O <sub>s</sub>	-0.82688	-0.46459	0	0		1.00000	0.84418	-16.11722		94.30	85.50	44.80	1.27343	0.06624
$\text{RH}_2\text{C}_s-\text{O}_2\text{S}(\text{O}_2)\text{OR}^*$	C <sub>s</sub>	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.58181	-16.35095	92.41	87.59	43.35	1.30512	0.03456
$(\text{C}-\text{O}(\text{iii}))$	C <sub>s</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$\text{C}-\text{H}(\text{CH}_3)$	C <sub>s</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$\text{C}-\text{H}(\text{CH}_3)$	C <sub>s</sub>	-0.92918	-0.92918	0	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$\text{C}-\text{H}(\text{CH})$	C <sub>s</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83579	0.38106
$\text{H}_3\text{C}_s\text{C}_s\text{H}_2\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$\text{H}_3\text{C}_s\text{C}_s\text{H}_2\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	0	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{R}-\text{H}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(\text{C}-\text{C}(\text{bi}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{R}-\text{H}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{e}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}^*)\text{HCH}_2-$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$(\text{C}-\text{C}(\text{d}))$	C <sub>s</sub>	-0.92918	-0.92918	-0.92918	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{RCH}_2\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{C}_s(\text{R}^*-\text{H}_2\text{C}_s)\text{CH}_2-$	C <sub>s</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	1			



Table 15.186. The energy parameters (eV) of functional groups of alkyl sulfates.

Parameters	C-O (i) Group	C-O (ii) Group	O-S Group	SO <sub>2</sub> Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$n_1$	1	1	1	4	3	2	1	1	1	1	1	1	1
$n_2$	0	0	0	0	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.85395	0.85395	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	0	1	0	1	1	0	0	0	1	1	0
$C_6$	2	2	2	8	1	1	1	2	2	2	2	2	2
$C_7$	0	0	0	1	3	2	1	0	0	0	0	0	0
$C_{10}$	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{11}$	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
$V_p$ (eV)	-33.15757	-33.47304	-48.93512	-180.36454	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_r$ (eV)	10.12103	10.15605	9.18680	39.92103	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T$ (eV)	9.17389	9.32537	14.36741	48.52397	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_a$ (eV)	-4.58695	-4.66268	-7.18371	-24.26198	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{(10^6 \text{ rad})}$ (eV)	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.55946	-15.56407	-15.55946	-15.55946
$\Delta E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-1.44915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0	0	0	0
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-13.18574	-12.98113	0.92918	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.55946	-15.56407	-15.55946	-15.55946
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-31.63533	-31.63544	-31.63543	-126.54154	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-1.44915	-1.65376	-0.92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-33.08452	-33.28912	-32.56455	-126.54147	-67.69450	-49.66493	-31.63537	-33.40373	-33.40373	-33.08452	-33.40373	-33.08452	-33.08452
$\omega (10^6 \text{ rad/s})$	22.0240	12.1583	33.4164	11.5378	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	15.4846	9.55643
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	14.49660	8.00277	21.99527	7.59437	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	10.19220	6.29021
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-0.24921	-0.18631	-0.30214	-0.17247	-0.23532	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	0.13663	0.13663	0.08679	0.12832	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	[21]	[21]	[42]	[43]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[2]	[4]	[5]	[2]	[2]	[2]
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-0.18089	-0.11799	-0.25875	-0.10831	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-33.26541	-33.40711	-32.82330	-126.97472	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.26541	-33.59732	-33.18712	-33.18712
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{10^6 \text{ rad}}^{\text{atom}} (eV)$	3.99563	4.13733	3.55352	8.61994	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.187. The total bond energies of alkyl sulfates calculated using the functional group composition and the energies of Table 15.186 compared to the experimental values [3].

Formula	Name	C-O (i) Group	C-O (ii) Group	O-S Group	SO <sub>2</sub> Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>4</sub> H <sub>9</sub> SO <sub>4</sub>	Dimethyl sulfate	2	0	2	1	2	0	0	0	0	0	0	0	0	48.734	48.734	0.00058
C <sub>4</sub> H <sub>9</sub> SO <sub>4</sub>	Diethyl sulfate	0	2	2	1	2	0	0	0	0	0	0	0	0	73.3077	73.346	0.00061
C <sub>4</sub> H <sub>9</sub> SO <sub>4</sub>	Dipropyl sulfate	0	2	2	1	2	0	0	0	0	0	0	0	0	97.6167	97.609	-0.00008



Table 15.188. The bond angle parameters of alkyl sulfates and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mp}^3, \text{AO})$ .

Atoms of angle	$2c_1$ Bond 1 ( $a_1$ )	$2c_2$ Bond 2 ( $a_2$ )	$2c_3$ Terminal Atom ( $a_3$ )	$F_{1, \text{terminal}}$ Atom 1 (Table 15.3.A)	Atom 1 Hybridization Designation (Table 15.3.A)	$F_{1, \text{terminal}}$ Atom 2 (Table 15.3.A)	Atom 2 Hybridization Designation (Table 15.3.A)	$S_1$ Atom 1	$S_2$ Atom 2	$C_1$	$C_2$	$\zeta_1$	$\zeta_2$	$E_T$ (eV)	$\theta_i$ (°)	$\theta_j$ (°)	$\theta_k$ (°)	Cal. $\theta$ (°)	Exp. $\theta$ (°)
$\angle O_1 N O_2$	2.72634	2.72634	4.7329	-15.95954 $O_1$	9	-15.95954 $O_2$	9	0.85252	0.85252	1	1	1	0.85252	-1.65376				120.44	120.9 [41] (dimethyl sulfate)
$\angle O_1 N O_3$	2.72634	2.96203	4.6690	-15.95954 $O_1$	9	-16.11722 $O_2$	11	0.85252	0.84418	1	1	1	0.84835	-1.65376				110.26	109.57 [41] (dimethyl sulfate)
$\angle O_1 N O_4$	2.96203	2.96203	4.6476	-16.11722 $O_1$	11	-16.11722 $O_2$	11	0.84418	0.84418	1	1	1	0.84418	-1.65376				103.35	103.85 [44] (dimethyl sulfate)
$\angle C_1 O_1 S$	2.68862	2.96203	4.8416	-15.75493 $C_1$	7	-10.34001 $S$	S	0.86359	0.7641 (Eq. (15.139))	1	0.7641 (Eq. (15.139))	1	0.82000	-0.72457				117.84	117.43 [41] (dimethyl sulfate)
Methylene $\angle HC_1 H$	2.11106	2.11106	3.4252	-15.75493 $C_1$	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_1 C_1 C_2$																			112 (propane) 113.8 (butane) 110.8 (isobutane) 111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_1 H$	2.09711	2.09711	3.4252	-15.75493 $C_1$	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_1 C_1 C_2$																		109.44	
$\angle C_1 C_1 H$																		109.44	
$\angle C_1 C_1 C_2$	2.91547	2.91547	4.7958	-16.68412 $C_1$	25	-16.68412 $C_2$	25	0.81549	0.81549	1	1	1	0.81549	-1.83836				110.67	110.8 (isobutane)
$\angle C_1 C_1 H$	2.91547	2.11323	4.1633	-15.55033 $C_1$	5	-14.82575 $C_2$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_1 C_1 H$	2.91547	2.09711	4.1633	-15.55033 $C_1$	5	-14.82575 $C_2$	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_1 C_1 C_2$	2.90327	2.90327	4.7958	-15.55033 $C_1$	5	-14.82575 $C_2$	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.83836				111.27	111.4 (isobutane)
$\angle C_1 C_1 C_2$													72.50					107.50	



# NITROALKANES ( $C_nH_{2n+2-m}(NO_2)_m$ , $n=1,2,3,4,5\ldots\infty$ )

The nitroalkanes,  $C_nH_{2n+2-m}(NO_2)_m$ , comprise a  $NO_2$  functional group and a  $C-N$  functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and  
 5 methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  
 10  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has  
 15 three unpaired electrons corresponding to the ground state  $^4S_{3/2}$ . The bonding in the nitro ( $NO_2$ ) functional group is similar to that in the  $SO_2$  group given previously. It also has similarities to the bonding in the carbonyl functional group. In the  $NO_2$  group, the two unpaired electrons of the  $O$  atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the  
 20 nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the  $C2sp^3$  HO. In nitroalkanes, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ , and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$  [38]. To meet the equipotential condition of the union of the  $N=O$   
 25  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $N=O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned}
 c_2(O \text{ to } N2p \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(N)} c_2(C2sp^3 HO) \\
 &= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}} (0.91771) \\
 &= 0.85987
 \end{aligned}
 \tag{15.140}$$



Since there are two *O* atoms in a linear combination that comprises the bonding of the  $NO_2$  group, the unpaired electrons of each *O* cancel each others effect such that  $E_{mag}$  is not subtracted from the total energy of  $NO_2$ . Additionally,  $E_T(atom-atom,msp^3.AO) = -3.71673\text{ eV} = 4(-0.92918\text{ eV})$  (Eq. (14.513)) is the maximum  
 5 given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The *C-N* group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and  $\Delta E_{H_2MO}(AO/HO) = -0.72457\text{ eV}$  for nitroalkane and  $\Delta E_{H_2MO}(AO/HO) = -1.44915\text{ eV}$  for  
 10 primary amines. Whereas,  $E_T(atom-atom,msp^3.AO) = -1.44915\text{ eV}$  for both functional groups. This condition matches the energy of the *C-N* group with the  $NO_2$  having  $\Delta E_{H_2MO}(AO/HO) = 0$ .

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and  
 15 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.192 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was  
 20 subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using Eqs. (15.79-15.108) are given in Table 15.194.

Table 15.189. The symbols of functional groups of nitroalkanes.

Functional Group	Group Symbol
$NO_2$ group	$NO_2$
<i>C-N</i>	<i>C-N</i>
$CH_3$ group	<i>C-H</i> ( $CH_3$ )
$CH_2$ group	<i>C-H</i> ( $CH_2$ )
<i>CH</i>	<i>C-H</i>
<i>CC</i> bond (n- <i>C</i> )	<i>C-C</i> (a)
<i>CC</i> bond (iso- <i>C</i> )	<i>C-C</i> (b)
<i>CC</i> bond (tert- <i>C</i> )	<i>C-C</i> (c)
<i>CC</i> (iso to iso- <i>C</i> )	<i>C-C</i> (d)
<i>CC</i> (t to t- <i>C</i> )	<i>C-C</i> (e)
<i>CC</i> (t to iso- <i>C</i> )	<i>C-C</i> (f)



Table 15.190. The geometrical bond parameters of nitroalkanes and experimental values [1].

Parameter	$\text{NO}_2$	$\text{C}-\text{N}$	$\text{C}-\text{H}$ ( $\text{CH}_3$ )	$\text{C}-\text{H}$ ( $\text{CH}_2$ )	$\text{C}-\text{C}$ (a)	$\text{C}-\text{C}$ (b)	$\text{C}-\text{C}$ (c)	$\text{C}-\text{C}$ (d)	$\text{C}-\text{C}$ (e)	$\text{C}-\text{C}$ (f)
$\alpha$ ( $^\circ$ )	1.33221	1.97794	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$\alpha'$ ( $^\circ$ )	1.15421	1.40639	1.04856	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ ( $\text{\AA}$ )	1.22157	1.48846	1.10974	1.11713	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length ( $\text{\AA}$ )	1.224 (nitromethane)	1.489 (nitromethane)	1.107 (C-H propane)	1.122 (isobutane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
$h_c$ ( $^\circ$ )	0.66526	1.39079	1.27295	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$\theta$	0.86039	0.71104	0.63380	0.63159	0.63095	0.63095	0.63095	0.63095	0.63095	0.63095

Table 15.191. The MO to HO intercept geometrical bond parameters of nitroalkanes.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mfp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C_{2sp}^*$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{Coulomb}}$ (eV) Final	$E^*(\text{C}_{2sp}^*)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$\text{RN(O)}=\text{O}$	O	-0.92918	0	0	0	-15.75493	0.86359	-15.75493	-15.75493	135.25	44.75	66.05	0.54089	0.61333
$\text{RN(O)}=\text{O}$	N	-0.92918	-0.92918	-0.72457	0	-17.40869	0.78155	-17.40869	-17.40869	131.57	48.43	61.50	0.63538	0.51864
$\text{H}_2\text{C}-\text{NO}_2$	C	-0.72457	0	0	0	-15.33033	0.97495	-15.33033	-15.33033	80.47	99.53	38.35	1.55123	0.14484
$\text{RH}_2\text{C}-\text{NO}_2$	N	-0.92918	-0.92918	-0.72457	0	-17.40869	0.78155	-17.40869	-17.40869	69.30	110.70	31.71	1.68259	0.27620
$\text{R}=\text{H, alkyl}$	C	-0.72457	-0.92918	0	0	-15.326945	0.91771	-15.326945	-15.326945	74.96	105.04	34.98	1.62061	0.21422
$\text{C}-\text{H}$ ( $\text{CH}_3$ )	C	-0.92918	0	0	0	-15.234487	0.86359	-15.234487	-15.234487	77.49	102.51	41.48	1.23564	0.18708
$\text{C}-\text{H}$ ( $\text{CH}_2$ )	C	-0.92918	0	0	0	-15.347406	0.91771	-15.347406	-15.347406	68.47	111.53	35.84	1.35486	0.22933
$\text{C}-\text{H}$ ( $\text{CH}$ )	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.77247	-15.440324	-15.440324	61.10	118.90	31.37	1.42988	0.37526
$\text{H}_2\text{C}-\text{C}-\text{H}_2$ ( $\text{C}-\text{C}$ )	C	-0.92918	0	0	0	-15.75493	0.86359	-15.75493	-15.75493	63.82	116.18	30.08	1.83879	0.38106
$\text{H}_2\text{C}-\text{C}-\text{H}_2$ ( $\text{C}-\text{C}$ )	C	-0.92918	-0.92918	-0.92918	0	-16.68412	0.81549	-16.68412	-16.68412	56.41	125.59	26.06	1.90590	0.45117
$\text{R}-\text{H}_2\text{C}-\text{C}-\text{H}_2$ ( $\text{C}-\text{C}$ )	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.77247	-15.440324	-15.440324	48.30	131.70	21.90	1.97162	0.51388
$\text{R}-\text{H}_2\text{C}-\text{C}-\text{H}_2$ ( $\text{C}-\text{C}$ )	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.77247	-15.440324	-15.440324	48.21	131.79	21.74	1.95734	0.50570
$\text{R}-\text{H}_2\text{C}-\text{C}-\text{H}_2$ ( $\text{C}-\text{C}$ )	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.77247	-15.440324	-15.440324	48.30	131.70	21.90	1.97162	0.51388
$\text{R}-\text{H}_2\text{C}-\text{C}-\text{H}_2$ ( $\text{C}-\text{C}$ )	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.77247	-15.440324	-15.440324	50.04	129.96	22.66	1.94462	0.49298
$\text{R}-\text{H}_2\text{C}-\text{C}-\text{H}_2$ ( $\text{C}-\text{C}$ )	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.77247	-15.440324	-15.440324	52.78	127.22	24.04	1.92443	0.47279
$\text{R}-\text{H}_2\text{C}-\text{C}-\text{H}_2$ ( $\text{C}-\text{C}$ )	C	-0.92918	-0.92918	-0.92918	0	-15.440324	0.77247	-15.440324	-15.440324	50.04	129.96	22.66	1.94462	0.49298



Table 15.192. The energy parameters (eV) of functional groups of nitroalkanes.

Parameters	$NO_2$ Group	$C-N$ Group	$CH_3$ Group	$CH_2$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$n_1$	2	1	3	2	1	1	1	1	1	1	1
$n_2$	0	0	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.85987	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	0	1	1	0	0	0	1	1	0
$C_6$	4	2	1	1	1	2	2	2	2	2	2
$C_7$	0	0	3	2	1	0	0	0	0	0	0
$C_8$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{10}$	1	1	1	1	1	1	1	1	1	1	1
$V_1$ (eV)	-106.90919	-31.36351	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_2$ (eV)	25.57588	9.67426	38.97278	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T_1$ (eV)	40.12475	7.92833	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m$ (eV)	-20.06238	-3.96416	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{1,10}$ (eV)	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,10}$ (eV)	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_{1,10}$ (eV)	0	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{1,10}$ (eV)	-63.27093	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$E_{1,10}$ (eV)	-3.71673	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{1,10}$ (eV)	-66.98746	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373	-33.49373
$\omega$ [ $10^{15}$ rad / s]	19.0113	10.5087	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.43699	9.43699
$E_{1,10}$ (eV)	12.51354	6.91703	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.21159	6.21159
$E_{1,10}$ (eV)	-0.23440	-0.17214	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16515	-0.16515
$E_{1,10}$ (eV)	0.19542	0.10539	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{1,10}$ (eV)	-0.13769	-0.11945	-0.22757	-0.14502	-0.07200	-0.10359	-0.10359	-0.15924	-0.10359	-0.10359	-0.10359
$E_{1,10}$ (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{1,10}$ (eV)	-67.26284	-33.20397	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24376	-33.59732	-33.59732	-33.59732
$E_{1,10}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{1,10}$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{1,10}$ (eV)	8.72329	3.93419	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.193. The total bond energies of nitroalkanes calculated using the functional group composition and the energies of Table 15.192 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{1,10}$  (eV) values based on composition is given by (15.38).

Formula	Name	$NO_2$ Group	$C-N$ Group	$CH_3$ Group	$CH_2$ Group	$CH$ Group	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	$E_{mag}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$CH_3NO_2$	Nitromethane	1	1	1	0	0	0	0	0	0	0	0	0	25.14934	25.107	-0.00168
$C_2H_5NO_2$	Nitroethane	1	1	1	1	0	0	0	0	0	0	0	0	37.30704	37.292	-0.00040
$C_3H_7NO_2$	1-Nitropropane	1	1	2	0	0	0	0	0	0	0	0	0	49.46474	49.451	-0.00028
$C_4H_9NO_2$	2-Nitropropane	1	2	0	1	0	0	0	0	0	0	0	0	49.56563	49.602	0.00074
$C_4H_9NO_2$	1-Nitrobutane	1	2	0	0	0	0	0	0	0	0	0	0	61.62244	61.601	-0.00036
$C_5H_{11}NO_2$	2-Nitropentane	1	3	0	0	0	0	0	0	0	0	0	0	61.90697	61.945	0.00061
$C_6H_{13}NO_2$	1-Nitrohexane	1	4	0	0	0	0	0	0	0	0	0	0	73.28014	73.259	-0.00028



Table 15.194. The bond angle parameters of nitroalkanes and experimental values [1]. In the calculation of  $\theta_2$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{usp}^3, \text{AO})$ .

Atoms of Angle	$2c^1$ Bond 1 ( $\theta_1$ )	$2c^2$ Bond 2 ( $\theta_2$ )	$2c^3$ Terminal Atom ( $\theta_3$ )	$E_{\text{calc}}^{\text{calc}}$ or $E^{\text{exp}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$c_1$ Atom 1	$c_2$ Atom 2	$c_3$ Atom 3	$C_1$	$C_2$	$\varphi$	$c_2^2$	$E_T$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle \text{N-C}_\alpha\text{-H}$	2.81279	2.09711	3.0665	-14.82575	1	0.91771	-14.53414		0.75	1	0.75	0.99312	0				106.87	107 (nitromethane)
$\angle \text{O}_\alpha\text{-N-O}_\beta$	2.30843	2.30843	4.1231	-16.68411	24	0.81549	-16.68411	$O_\beta$	1	1	1	0.81549	-1.44915				126.52	125.3 (nitromethane)
$\angle \text{H-C}_\alpha\text{-H}$	2.11106	2.11106	3.4252	-15.75493	7	0.86359		H	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$														69.51			110.49	112 (propane) 115.8 (butane) 110.8 (isobutane)
$\angle \text{C}_\alpha\text{-C}_\beta\text{-H}$														69.51			110.49	111.0 (butane) 111.4 (isobutane)
$\angle \text{H-C}_\alpha\text{-C}_\beta$	2.09711	2.09711	3.4252	-15.75493	7	0.86359		H	1	1	0.75	1.15796	0				109.50	
$\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$														70.56			109.44	
$\angle \text{C}_\alpha\text{-C}_\beta\text{-H}$														70.56			109.44	
$\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$	2.91547	2.91547	4.7958	-16.68412	25	0.81549	-16.68412	$C_\gamma$	1	1	1	0.81549	-1.53836				110.67	110.8 (isobutane)
$\angle \text{C}_\alpha\text{-C}_\beta\text{-H}$	2.91547	2.11323	4.1633	-15.55033	5	0.87495	-14.82575	$C_\gamma$	0.75	1	0.75	1.04887	0				110.76	
$\angle \text{C}_\alpha\text{-C}_\beta\text{-H}$	2.91547	2.09711	4.1633	-15.55033	5	0.87495	-14.82575	$C_\gamma$	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$	2.90327	2.90327	4.7958	-15.55033	5	0.87495	-14.82575	$C_\gamma$	0.75	1	0.75	1.04887	-1.53836				111.27	111.4 (isobutane)
$\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$														72.50			107.50	



# ALKYL NITRITES ( $C_nH_{2n+2-m}(NO_2)_m$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl nitrites,  $C_nH_{2n+2-m}(NO_2)_m$ , comprise a  $RC-O-NO$  moiety that comprises  $C-O$ ,  $O-N$ , and  $NO$  functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise 5 methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, 10 and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  $^4S_{3/2}$ . The bonding in the nitro ( $NO$ ) functional group is similar to that in the  $SO$  group given previously. It also has similarities to the bonding in the carbonyl functional group. In the  $NO$  group, the two unpaired electrons of the  $O$  atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the  $O-N$  functional 20 group that is further energy matched to the  $C2sp^3$  HO of the  $C-O$  functional group. To meet the equipotential condition of the union of the  $N=O$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the  $N=O$ -bond MO given by Eq. (15.140) is  $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$ .

As in the case of the carbonyl group, two unpaired  $O$  electrons result upon bond 25 breakage of the  $N=O$  bond which requires that two times  $E_{mag}$  of oxygen (Eq. (15.59)) be subtracted from the total energy of  $NO$ . Additionally,  $E_r(atom - atom, msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are equal to  $-0.92918 \text{ eV}$  (Eq. (14.513)) which matches the energy of the  $N=O$  bond with the contiguous  $O-N$  bond and matches the energy contribution of an oxygen atom.



The  $O-N$  functional group comprise a single-bond,  $H_2$ -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the  $C2sp^3$  HO of the  $C-O$  functional group. In alkyl nitrites, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-O$ -bond MO given by Eq. 5 (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ . The hybridization factor  $c_2$  of Eq. (15.52) for a  $C-N$ -bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ . Thus, the hybridization factor  $c_2$  of Eq. (15.52) for  $O-N$  that bridges the  $C-O$  and  $N=O$  bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727 \quad (15.141)$$

10  $E_r(atom - atom, msp^3)AO = -0.92918 \text{ eV}$  in order to match the energy of the  $NO$  group and  $E(AO / HO) = -15.35946 \text{ eV}$  in order to match the  $C-O$  functional group.

The  $C-O$  functional group is equivalent to that of an ether as given in the corresponding section except that  $E_r(atom - atom, msp^3)AO$  and  $\Delta E_{H_2MO}(AO / HO)$  are both  $-0.72457 \text{ eV}$  which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 20 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.



Table 15.195. The symbols of functional groups of alkyl nitrites.

Functional Group	Group Symbol
NO group	NO
O-N	O-N
C-O	C-O
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C-C' (a)
CC bond (iso-C)	C-C' (b)
CC bond (tert-C)	C-C' (c)
CC (iso to iso-C)	C-C' (d)
CC (t to t-C)	C-C' (e)
CC (t to iso-C)	C-C' (f)

Table 15.196. The geometrical bond parameters of alkyl nitrites and experimental values [1].

Parameter	NO Group	O-N Group	C-O Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a$ (Å)	1.32255	1.76440	1.85327	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.15002	1.32831	1.36135	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'$ (Å)	1.21713	1.40582	1.44079	1.10974	1.11713	1.11827	1.54280	1.54280	1.55635	1.54280	1.55635	1.55635
Exp. Bond Length (Å)	1.205 (methyl nitrate) 1.2 (HNO <sub>2</sub> )	1.402 (methyl nitrate) 1.432 (HNO <sub>2</sub> )	1.437 (methyl nitrate)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c$ (Å)	0.65314	1.16134	1.25751	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$\sigma$	0.86955	0.75284	0.73457	0.63580	0.63159	0.65095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15 197. The MO to HO intercept geometrical bond parameters of alkyl nitriles.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{map}^2, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy (eV)	$r_{\text{final}}$ (a <sub>0</sub> )	$r_{\text{final}}$ (a <sub>0</sub> )	$E_{\text{calculated}}$ (eV) Final	$E(\text{C}2\text{sp}^2)$ (eV) Final	$\theta'$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
$RON=O$	O	-0.46459	0	0	0	-15.20834	1.00000	0.88993	-15.20834		137.15	42.85	67.90	0.9764	0.63238
$RON=O$	N	-0.46459	-0.46459	0	0	-15.75493	0.93084	0.86359	-15.75493		136.09	43.91	66.48	0.92781	0.62221
$RO_2=NO_2$	O <sub>1</sub>	-0.46459	-0.36229	0	0	-15.63263	1.00000	0.86923	-15.63263		99.22	80.78	47.63	1.18905	0.19325
$RO_2=NO_2$	N	-0.46459	-0.46459	0	0	-15.75493	0.93084	0.86359	-15.75493		98.78	81.22	47.30	1.19655	0.13175
$RH_2C=O_2NO_2$	O <sub>1</sub>	-0.36229	-0.46459	0	0	-15.63263	1.00000	0.86923	-15.63263		91.43	88.57	43.71	1.33962	0.02173
$H_2C=O_2NO_2$	C	-0.36229	0	0	0	-15.197708	0.91771	0.89582	-15.18804	-14.99717	93.71	86.29	45.31	1.30342	0.05793
$-CH_2H_2C=O_2NO_2$	C	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	89.16	90.84	42.16	1.37373	0.01238
$C-H(C_1)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H(C_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.08412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H(C_3)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_2C_2H_2CH_2CH_2-$ (C-C (a))	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.33879	0.38106
$H_2C_2H_2CH_2CH_2-$ (C-C (b))	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.08412	-16.49325	56.41	123.59	26.06	1.30890	0.43117
$R-H_2C(R'-H_2C)(R'')HCH_2-$ (C-C (c))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C(R'-H_2C)(R'')HCH_2-$ (C-C (d))	C	-0.92918	-0.72457	-0.72457	-0.72457	-154.17660	0.91771	0.73869	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$rac(H_2C_2H_2CH_2CH_2-)$ (C-C (e))	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$rac(H_2C_2H_2CH_2CH_2-)$ (C-C (f))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.67665	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$rac(H_2C_2H_2CH_2CH_2-)$ (C-C (g))	C	-0.72457	-0.92918	-0.92918	0	-154.19663	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$rac(H_2C_2H_2CH_2CH_2-)$ (C-C (h))	C	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.67665	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.198. The energy parameters (eV) of functional groups of alkyl nitriles.

Parameters	NO Group	O-N Group	C-O Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\eta_1$	2	1	1	3	2	1	1	1	1	1	1	1
$\eta_2$	0	0	0	2	1	0	0	0	0	0	0	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0	0	0
$C_1'$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2'$	1	1	1	1	1	1	1	1	1	1	1	1
$C_3'$	1	1	1	1	1	1	1	1	1	1	1	1
$C_4'$	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5'$	2	0	0	0	1	1	0	0	0	1	1	0
$C_6'$	4	2	2	1	1	1	2	2	2	2	2	2
$C_7'$	0	0	0	3	2	1	0	0	0	0	0	0
$C_{in}$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{out}$	1	1	1	1	1	1	1	1	1	1	1	1
$V_c$ (eV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214
$V_r$ (eV)	23.66182	20.48593	9.94536	38.92728	25.78002	12.87680	9.33352	9.33352	9.33352	9.33352	9.33352	9.33352
$T_r$ (eV)	40.95920	12.13739	8.64465	32.53914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464	6.77464
$V_m$ (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732
$E_{(w,m)}$ (eV)	0	-15.35946	-14.63489	-15.36407	-15.36407	-14.63489	-15.36407	-15.36407	-15.36407	-15.36407	-15.36407	-15.36407
$\Delta E_{(w,m)}$ (eV)	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_{(w,m)}$ (eV)	0.92918	-15.35946	-13.91032	-15.36407	-15.36407	-14.63489	-15.36407	-15.36407	-15.36407	-15.36407	-15.36407	-15.36407
$E_{(w,m)}$ (eV)	-63.27057	-31.63527	-31.63537	-67.69451	-49.66495	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$F_r$ (atom - atom, $mnp^*, d(t)$ ) (eV)	-0.92918	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836	-1.85836
$F_r$ (eV)	-64.19992	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49573	-33.49573	-33.49573	-33.49573	-33.49573	-33.49573
$\omega$ ( $10^5$ rad/s)	19.2199	23.3578	20.7301	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.43699	9.43699
$F_r$ (eV)	12.65089	15.37450	13.64490	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
$\bar{E}_r$ (eV)	-0.22587	0.25261	-0.23648	-0.23532	-0.25017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515	-0.16515
$\bar{F}_{rm}$ (eV)	0.20396	0.10725	0.13663	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
$\bar{E}_{rm}$ (eV)	[46]	[47]	[21]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[4]	[4]	[4]	[4]	[4]	[4]
$\bar{E}_{rm}$ (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07256	-0.10359	-0.10359	-0.10359	-0.10359
$\bar{E}_{rm}$ (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$\bar{E}_{rm}$ (eV)	-64.44771	32.76354	-32.52811	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732
$\bar{E}_{rm}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$\bar{E}_{rm}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$\bar{E}_{rm}$ (eV)	5.67933	3.49376	3.25833	12.49186	7.83016	3.37601	4.32754	4.29921	4.29921	4.17951	3.62128	3.91734

Table 15.199. The total bond energies of alkyl nitriles calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula	NO Group	O-N Group	C-O Group	CH <sub>3</sub> Group	CH <sub>2</sub> Group	CH Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> NO <sub>2</sub>	1	1	1	1	0	0	0	0	0	0	0	0	24.9328	24.955	0.00126



Table 15.200. The bond angle parameters of alkyl nitrites and experimental values [1]. In the calculation of  $\theta_p$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{ang}^3 \cdot \text{AO})$ .

Atom of angle	$2c'$ Bond 1 ( $\text{AO}$ )	$2c''$ Bond 2 ( $\text{AO}$ )	$2c'''$ Terminal Atom ( $\text{AO}$ )	$E_{\text{residue}}$ Atom 1 or $E_{\text{residue}}$ Atom 2	Atom 1 Hybridization Designation (Table 15.3.A)	$c_1$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$\phi_1$	$\phi_2$	$\theta_p$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle \text{CO}_2\text{N}$	2.72270	2.65661	4.4944	-16.68412 $C_s$	N	0.81549	0.91140 (Eq. (15.11.6))	I	I	I	0.86345	-1.44915			113.33	
$\angle \text{O}_2\text{NO}_2$	2.30004	2.65661	4.1231	-16.68411 $O_h$	24	0.81549	0.81549	I	I	I	0.81549	-1.44915			112.38	110.7 ( $\text{HNO}_2$ )
Methylene $\angle \text{HC}_2\text{H}$	2.11106	2.11106	3.4252	-15.75493 $H$	H	0.86359	I	I	I	0.75	1.15796	0			108.44	107 (propane)
$\angle C'_s C'_s C'_s$															112	
$\angle C'_s C'_s H$													69.51		110.49	113.8 (propane) 113.8 (butane) 110.8 (isobutane)
Methyl $\angle \text{HC}_2\text{H}$	2.09711	2.09711	3.4252	-15.75493 $H$	H	0.86359	I	I	I	0.75	1.15796	0			109.50	111.0 (butane) 111.4 (isobutane)
$\angle C'_s C'_s C'_s$															109.44	
$\angle C'_s C'_s H$															109.44	
$\angle C'_s C'_s C'_s$	2.91547	2.91547	4.7958	-16.68412 $C_s$	25	0.81549	0.81549	I	I	I	0.81549	-1.83836			110.67	110.8 (isobutane)
$\angle C'_s C'_s H$	2.91547	2.11323	4.1633	-15.55033 $C_s$	5	0.87495	0.91771	0.75	I	0.75	1.04887	0			110.76	
$\angle C'_s C'_s H$	2.91547	2.09711	4.1633	-15.55033 $C_s$	5	0.87495	0.91771	0.75	I	0.75	1.04887	0			111.27	111.4 (isobutane)
$\angle C'_s C'_s C'_s$	2.90327	2.90327	4.7958	-15.55033 $C_s$	5	0.87495	0.91771	0.75	I	0.75	1.04887	-1.83836			111.27	111.4 (isobutane)
$\angle C'_s C'_s C'_s$													72.50		107.50	



# ALKYL NITRITES ( $C_nH_{2n+2-m}(NO_2)_m$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl nitrites,  $C_nH_{2n+2-m}(NO_2)_m$ , comprise a  $RC-O-NO$  moiety that comprises  $C-O$ ,  $O-N$ , and  $NO$  functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise 5 methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, 10 and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  $^4S_{3/2}^0$ . The bonding in the nitro ( $NO$ ) functional group is similar to that in the  $SO$  group given previously. It also has similarities to the bonding in the carbonyl functional group. In the  $NO$  group, the two unpaired electrons of the  $O$  atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the  $O-N$  functional 20 group that is further energy matched to the  $C2sp^3$  HO of the  $C-O$  functional group. To meet the equipotential condition of the union of the  $N=O$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the  $N=O$ -bond MO given by Eq. (15.140) is  $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$ .

As in the case of the carbonyl group, two unpaired  $O$  electrons result upon bond 25 breakage of the  $N=O$  bond which requires that two times  $E_{mag}$  of oxygen (Eq. (15.59)) be subtracted from the total energy of  $NO$ . Additionally,  $E_r(atom-atom,msp^3.AO)$  and  $\Delta E_{H_1MO}(AO/HO)$  are equal to  $-0.92918 \text{ eV}$  (Eq. (14.513)) which matches the energy of the  $N=O$  bond with the contiguous  $O-N$  bond and matches the energy contribution of an oxygen atom.



The  $O-N$  functional group comprise a single-bond,  $H_2$ -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the  $C2sp^3$  HO of the  $C-O$  functional group. In alkyl nitrites, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-O$ -bond MO given by Eq. 5 (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ . The hybridization factor  $c_2$  of Eq. (15.52) for a  $C-N$ -bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ . Thus, the hybridization factor  $c_2$  of Eq. (15.52) for  $O-N$  that bridges the  $C-O$  and  $N=O$  bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727 \quad (15.141)$$

10  $E_T(atom - atom, msp^3.AO) = -0.92918 \text{ eV}$  in order to match the energy of the  $NO$  group and  $E(AO / HO) = -15.35946 \text{ eV}$  in order to match the  $C-O$  functional group.

The  $C-O$  functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom - atom, msp^3.AO)$  and  $\Delta E_{H_2MO}(AO / HO)$  are both  $-0.72457 \text{ eV}$  which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 20 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.



Table 15.195. The symbols of functional groups of alkyl nitriles.

Functional Group	Group Symbol
NO group	NO
O-N	O-N
C-O	C-O
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.196. The geometrical bond parameters of alkyl nitriles and experimental values [1].

Parameter	NO Group	O-N Group	C-O Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$a$ (Å)	1.32255	1.76440	1.85327	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (Å)	1.15002	1.52831	1.36135	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length												
$2c'$ (Å)	1.21713	1.40582	1.44079	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.205 (methyl nitrate) 1.2 (HNO <sub>2</sub> )	1.402 (methyl nitrate) 1.432 (HNO <sub>2</sub> )	1.437 (methyl nitrate)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c'$ (Å)	0.65314	1.16134	1.25751	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.86955	0.75284	0.73457	0.63380	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nitriles.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mp}^2, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy ( $\text{C}^2\text{sp}^3$ ) (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{calculated}}$ (eV) Final	$E(\text{C}^2\text{sp}^3)$ (eV) Final	$\theta$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$\text{RON}=\text{O}$	O	-0.46459	0	0	0		1.00000	0.89943	-15.29034		137.15	42.85	67.90	0.99764	0.65238
$\text{RON}=\text{O}$	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.73493		136.09	43.91	66.48	0.92281	0.62221
$\text{RON}=\text{NO}_2$	O <sub>2</sub>	-0.46459	-0.36229	0	0		1.00000	0.86923	-15.63263		99.22	80.78	47.63	1.18005	0.19925
$\text{RON}=\text{NO}_2$	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.73493		98.78	81.22	47.30	1.19655	0.13175
$\text{RH}_2\text{C}=\text{O}, \text{NO}_2$	O <sub>2</sub>	-0.36229	-0.46459	0	0		1.00000	0.86923	-15.63263		91.45	88.57	43.71	1.33962	0.02173
$\text{RH}_2\text{C}=\text{O}, \text{NO}_2$	C <sub>2</sub>	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	93.71	86.29	45.31	1.30342	0.05793
$\text{CH}_2\text{H}_2\text{C}=\text{O}, \text{NO}_2$	C <sub>2</sub>	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	89.16	90.84	42.16	1.37373	0.01238
$\text{C}-\text{H}(\text{CH}_3)$	C <sub>1</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$\text{C}-\text{H}(\text{CH}_3)$	C <sub>1</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$\text{C}-\text{H}(\text{CH}_3)$	C <sub>1</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$\text{H}_3\text{C}-\text{C}(\text{H})\text{CH}_2-\text{CH}_2-$ (C-C (a))	C <sub>2</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.59106
$\text{H}_3\text{C}-\text{C}(\text{H})\text{CH}_2-\text{CH}_2-$ (C-C (b))	C <sub>2</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$\text{R}-\text{H}_2\text{C}-\text{C}(\text{H})\text{CH}_2-\text{CH}_2-$ (C-C (c))	C <sub>2</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{R}-\text{H}_2\text{C}-\text{C}(\text{H})\text{CH}_2-\text{CH}_2-$ (C-C (d))	C <sub>2</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.73889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$\text{R}-\text{H}_2\text{C}-\text{C}(\text{H})\text{CH}_2-\text{CH}_2-$ (C-C (e))	C <sub>2</sub>	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$\text{R}-\text{H}_2\text{C}-\text{C}(\text{H})\text{CH}_2-\text{CH}_2-$ (C-C (f))	C <sub>2</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.11599	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$\text{R}-\text{H}_2\text{C}-\text{C}(\text{H})\text{CH}_2-\text{CH}_2-$ (C-C (g))	C <sub>2</sub>	-0.72457	-0.92918	-0.92918	0	-154.19663	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$\text{R}-\text{H}_2\text{C}-\text{C}(\text{H})\text{CH}_2-\text{CH}_2-$ (C-C (h))	C <sub>2</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.11599	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298



Table 15.198. The energy parameters (eV) of functional groups of alkyl nitriles.

Parameters	NO	O-N	C-O	H <sub>2</sub>	H <sub>3</sub>	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
$n_1$	2	1	1	2	3	1	1	1	1	1	1	1
$n_2$	0	0	0	2	2	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0	0
$c_1$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$c_2$	1	1	1	1	1	1	1	1	1	1	1	1
$c_3$	1	1	1	1	1	1	1	1	1	1	1	1
$c_4$	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$c_5$	2	0	0	0	0	1	0	0	0	1	1	0
$c_6$	4	2	2	1	1	1	2	2	2	2	2	2
$c_7$	0	0	0	3	3	1	0	0	0	0	0	0
$c_{in}$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$c_{2u}$	1	1	1	1	1	1	1	1	1	1	1	1
$V_c$ (eV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-28.79214	-28.79214	-28.79214	-29.10112
$V_p$ (eV)	23.66182	20.48593	9.9436	38.92728	25.78002	12.87680	9.33532	9.33532	9.33532	9.33532	9.33532	9.37273
$T$ (eV)	40.95920	12.13739	8.64465	32.53914	21.06675	10.48582	6.77464	6.77464	6.77464	6.77464	6.77464	6.90500
$V_m$ (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10.53537	-5.24291	-3.38732	-3.38732	-3.38732	-3.38732	-3.38732	-3.45250
$E_{\text{ion}}^{\text{calc}}$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.35946
$\Delta E_{\text{HOMO}}$ (eV)	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_{\text{HOMO}}$ (eV)	0.92918	-15.35946	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.35946
$E_{\text{LUMO}}$ (eV)	-63.27057	-31.63537	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63535
$E_{\text{HOMO}} - \text{atom. nsp. At}$ (eV)	-0.92918	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.85836	-1.85836	-1.44915	-1.44915
$E_{\text{HOMO}}$ (eV)	-64.19992	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.49373	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^5 \text{ rad/s}$ )	19.2199	23.3578	20.7301	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.55643	9.55643
$E_{\text{HOMO}}$ (eV)	12.65089	15.37450	13.64490	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.29021	6.29021
$E_{\text{LUMO}}$ (eV)	-0.22587	0.25261	-0.25648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.16515	-0.16515	-0.16416	-0.16416
$E_{\text{HOMO}}$ (eV)	0.20396	0.10725	0.13663	0.35532	0.35532	0.35532	0.12312	0.12312	0.12312	0.12312	0.12312	0.12312
$E_{\text{HOMO}}$ (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.10359	-0.10359	-0.10260	-0.10260
$E_{\text{HOMO}}$ (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\text{HOMO}}$ (eV)	-64.44771	32.76354	-32.52811	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.59732	-33.59732	-33.59732	-33.18712
$E_{\text{HOMO}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{HOMO}}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\text{HOMO}}$ (eV)	5.67933	3.49376	3.25833	12.49186	7.83016	3.32601	4.37754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.199. The total bond energies of alkyl nitriles calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula	Name	NO	O-N	C-O	H <sub>2</sub>	H <sub>3</sub>	CH	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energies (eV)	Experimental Total Bond Energies (eV)	Relative Error
CH <sub>3</sub> NO <sub>2</sub>	Methyl nitrite	1	1	1	1	1	0	0	0	0	0	0	0	24.9328	24.955	0.00126



- Atoms of Angle	$2c^1$ Bond 1 $(a_b)$	$2c^2$ Bond 2 $(a_b)$	$2c^*$ Terminal Atoms $(a_s)$	$F_1^{(orb)}$ or $E_{orb}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{orb}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$\zeta_c^*$	$E_T$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_i$ ( $^\circ$ )	$\theta_z$ ( $^\circ$ )	Cal $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle CO_N N$	2.72270	2.65661	4.4944	-16.68412 $C_k$	25	-14.53414 $N$	N	0.81549	0.91140 (Eq. 15.116)	I	I	I	0.86545	-1.44915				113.33	
$\angle O_N MO_h$	2.30004	2.65661	4.1231	-16.68411 $O_n$	24	-16.68411 $O_h$	24	0.81549	0.81549	I	I	I	0.81549	-1.44915				112.38	110.7 ( $HNO_3$ )
Methylenes $\angle HC_H H$	2.11106	2.11106	3.4252	-15.75493 $O_n$	7	H	H	0.86359	I	I	I	0.75	1.15796	0				108.44	107 (propene)
$\angle C_C^* C_C^* C_C^*$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane) 111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_C^* H$	2.09711	2.09711	3.4252	-15.75493 $O_n$	7	H	H	0.86359	I	I	I	0.75	1.15796	0				109.50	
$\angle C_C^* C_C^* C_C^*$															70.56			109.44	
$\angle C_C^* C_C^* H$															70.56			109.44	
$\angle C_C^* C_C^* C_C^*$ iso $C_u$	2.91547	2.91547	4.7958	-16.68412 $C_k$	25	-16.68412 $C_e$	25	0.81549	0.81549	I	I	I	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_C^* C_C^* H$ iso $C_u$	2.91547	2.11323	4.1633	-15.53033 $C_u^*$	5	-14.82575 $C_k^*$	I	0.87495	0.91771	0.75	I	0.75	1.04887	0				110.76	
$\angle C_C^* C_C^* H$ iso $C_u$	2.91547	2.09711	4.1633	-15.53033 $C_u^*$	5	-14.82575 $C_k^*$	I	0.87495	0.91771	0.75	I	0.75	1.04887	0				111.4 (isobutane)	
$\angle C_C^* C_C^* C_C^*$ tert $C_u$	2.90327	2.90327	4.7958	-15.53033 $C_k$	5	-14.82575 $C_e$	I	0.87495	0.91771	0.75	I	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_C^* C_C^* C_C^*$															72.50			107.50	



# ALKYL NITRATES ( $C_n H_{2n+2-m} (NO_2)_m$ , $n = 1, 2, 3, 4, 5, \dots, \infty$ )

The alkyl nitrates,  $C_n H_{2n+2-m} (NO_2)_m$ , comprise a  $RC-O-NO_2$  moiety that comprises  $C-O$ ,  $O-N$ , and  $NO_2$  functional groups. The alkyl portion of the alkyl nitrate may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The  $NO_2$  functional group is equivalent to that of nitro alkanes with the exception that  $\Delta E_{H_2MO}(AO/HO)$  as well as  $E_T(atom-atom, msp^3.AO)$  is equal to  $-3.71673 \text{ eV}$  in order to match the group energy to that of the contiguous  $O-N$  bond. Furthermore, the  $O-N$  group with  $E_T(atom-atom, msp^3.AO) = -0.92918 \text{ eV}$  is equivalent to that of nitrites as given in the corresponding section.

The  $C-O$  functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom-atom, msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are both  $-0.92918 \text{ eV}$  which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.79-15.108) are given in Table 15.206.



Table 15.201. The symbols of functional groups of alkyl nitrates.

Functional Group	Group Symbol
NO <sub>2</sub> group	NO <sub>2</sub>
O-N	O-N
C-O	C-O
CH <sub>3</sub> group	C-H (CH <sub>3</sub> )
CH <sub>2</sub> group	C-H (CH <sub>2</sub> )
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.202. The geometrical bond parameters of alkyl nitrates and experimental values [1].

Parameter	NO <sub>2</sub> Group	O-N Group	C-O Group	C-H (CH <sub>3</sub> ) Group	C-H (CH <sub>2</sub> ) Group	C-H Group	C-C (a) Group	C-C (b) Group	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C (f) Group
$\alpha$ (°)	1.29538	1.76440	1.83991	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'$ (°)	1.13815	1.32831	1.35643	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (Å)	1.20456	1.40582	1.43559	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.205 (methyl nitrate) 1.2 (HNO <sub>2</sub> )	1.402 (methyl nitrate) 1.432 (HNO <sub>2</sub> )	1.437 (methyl nitrate)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,c$ (°)	0.61857	1.16134	1.24312	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
$e$	0.87862	0.75284	0.73723	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888



Table 15.203. The MO to HO intercept geometrical bond parameters of alkyl nitrates.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C_{2sp^2}$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E(\text{Final})$ (eV)	$\theta$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$RN(O)=O$	O	-0.92918	0	0	0	-15.75493	0.86359	0.86359	-15.75493	138.49	41.51	67.70	0.49144	0.64071
$RN(O)=O$	N	-0.92918	-0.92918	-0.46459	0	-17.14870	0.79540	0.79540	-17.14870	135.60	44.40	63.83	0.37133	0.56082
$RO_2-N(O)_2$	O <sub>1</sub>	-0.46459	-0.46459	0	0	-15.75493	0.86359	0.86359	-15.75493	98.78	81.22	47.30	1.19635	0.13175
$RO_2-N(O)_2$	N	-0.46459	-0.92918	-0.92918	0	-17.14870	0.79540	0.79540	-17.14870	92.78	87.22	43.03	1.28978	0.03852
$RH_2C_2-O_2N(O)_2$	O <sub>1</sub>	-0.46459	-0.46459	0	0	-15.75493	0.86359	0.86359	-15.75493	92.13	87.87	43.96	1.32431	0.03212
$R=H, \text{ allyl}$	O <sub>1</sub>	-0.46459	-0.46459	0	0	-15.75493	0.86359	0.86359	-15.75493	92.13	87.87	43.96	1.32431	0.03212
$H_2C_2-O_2N(O)_2$	C <sub>1</sub>	-0.46459	0	0	0	-152.08028	0.91771	0.88963	-15.20934	94.36	85.64	45.54	1.28972	0.06771
$-CH_2H_2C_2-O_2N(O)_2$	C <sub>1</sub>	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21952	89.90	90.10	42.44	1.35787	0.00143
$C-H (CH_2)$	C <sub>1</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	77.49	102.51	41.48	1.23564	0.18708
$C-H (CH_2)$	C <sub>1</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	68.47	111.53	35.84	1.35486	0.29933
$C-H (CH)$	C <sub>1</sub>	-0.92918	-0.92918	-0.92918	0	-154.40524	0.91771	0.77247	-17.61330	61.10	118.90	31.37	1.42988	0.37326
$H_2C_2H_2CH_2-$ (C-C (a))	C <sub>1</sub>	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	63.82	116.18	30.08	1.83879	0.38106
$H_2C_2H_2CH_2-$ (C-C (a))	C <sub>1</sub>	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_2C_2(R'-H_2C_2-R)HCH_2-$ (C-C (b))	C <sub>1</sub>	-0.92918	-0.92918	-0.92918	0	-154.40524	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_2C_2(R'-H_2C_2-R)HCH_2-$ (C-C (c))	C <sub>1</sub>	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	48.21	131.79	21.74	1.95734	0.50570
$HOOC_2C_2(H_2C_2-R)HCH_2-$ (C-C (d))	C <sub>1</sub>	-0.92918	-0.92918	-0.92918	0	-154.40524	0.91771	0.77247	-17.61330	48.30	131.70	21.90	1.97162	0.51388
$HOOC_2C_2(R'-H_2C_2-R)HCH_2-$ (C-C (e))	C <sub>1</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	50.04	129.96	22.66	1.94462	0.49298
$HOOC_2C_2(H_2C_2-R)HCH_2-$ (C-C (f))	C <sub>1</sub>	-0.72457	-0.92918	-0.92918	0	-154.19863	0.91771	0.78155	-17.40869	52.78	127.22	24.04	1.92443	0.47279
$HOOC_2C_2(R'-H_2C_2-R)HCH_2-$ (C-C (f))	C <sub>1</sub>	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	50.04	129.96	22.66	1.94462	0.49298



Table 15.204. The energy parameters (eV) of functional groups of alkyl nitrates.

Parameters	$\text{NO}_2$	O-N	C-O	$\text{CH}_3$	$\text{CH}_2$	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)
Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
$n_1$	2	1	1	3	2	1	1	1	1	1	1	1
$n_2$	0	0	0	2	1	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_2$	1	1	1	1	1	1	1	1	1	1	1	1
$C_3$	1	1	1	1	1	1	1	1	1	1	1	1
$C_4$	0.85987	1.06727	0.85593	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$C_5$	0	0	0	0	1	1	0	0	0	1	1	0
$C_6$	4	2	2	1	1	1	2	2	2	2	2	2
$C_7$	0	0	0	3	2	1	0	0	0	0	0	0
$C_8$	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_9$	1	1	1	1	1	1	1	1	1	1	1	1
$F_1$ (eV)	-112.63415	-42.85043	-32.35681	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$F_2$ (eV)	23.90868	20.48593	10.03058	38.92728	25.78002	12.87680	9.3352	9.3352	9.3352	9.3352	9.3352	9.3352
$F_3$ (eV)	43.47534	12.13759	8.79504	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$F_4$ (eV)	-21.75767	-6.66870	-4.59652	-16.26957	-10.55337	-5.34291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$\Delta E_{1,2,3,4,5,6,7,8,9}$ (eV)	-3.71673	0	-0.92918	0	0	0	0	0	0	0	0	0
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	3.71673	-15.35946	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407	-15.56407
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	-63.27107	-31.63527	-31.63542	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537	-31.63537
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	-3.71673	-0.92918	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	-66.98746	-32.56455	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega$ ( $10^{15}$ rad/s)	19.8278	23.3578	21.0910	24.9286	24.2751	24.1759	9.43699	9.43699	9.43699	9.43699	9.43699	9.43699
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	13.05099	15.37450	13.88249	16.40846	15.97831	15.91299	6.21159	6.21159	6.21159	6.21159	6.21159	6.21159
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	-0.23938	0.25261	-0.24004	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	0.19342	0.10725	0.13663	0.35532	0.35532	0.35532	0.12312	0.12312	0.09944	0.12312	0.12312	0.12312
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	[45]	[47]	[21]	( $E_0$ , (13.458))	( $E_0$ , (13.458))	( $E_0$ , (13.458))	[2]	[4]	[5]	[2]	[2]	[2]
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	-0.14267	0.19899	-0.17172	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	-67.27281	32.76554	-32.73627	-67.92207	-49.80996	-31.70737	-33.59732	-33.59732	-33.24376	-33.59732	-33.18712	-33.18712
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{1,2,3,4,5,6,7,8,9}$ (eV)	8.73325	3.49376	3.46649	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.205. The total bond energies of alkyl nitrates calculated using the functional group composition and the energies of Table 15.204 compared to the experimental values [3].

Formula	Name	$\text{NO}_2$	O-N	C-O	$\text{CH}_3$	$\text{CH}_2$	C-H	C-C (a)	C-C (b)	C-C (c)	C-C (d)	C-C (e)	C-C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$\text{CH}_3\text{NO}_2$	Methyl nitrate	1	1	1	1	0	0	0	0	0	0	0	0	38.117	38.117	-0.00244
$\text{C}_2\text{H}_5\text{NO}_2$	Ethyl nitrate	1	1	1	1	1	0	0	0	0	0	0	0	40.386	40.386	0.00151
$\text{C}_3\text{H}_7\text{NO}_2$	Propyl nitrate	1	1	1	1	2	0	0	0	0	0	0	0	52.5076	52.5076	0.00033
$\text{C}_4\text{H}_9\text{NO}_2$	Isopropyl nitrate	1	1	1	2	0	1	0	0	0	0	0	0	52.60168	52.725	0.00233



Table 15.206. The bond angle parameters of alkyl nitrates and experimental values [1]. In the calculation of  $\theta_e$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{AO})$ .

Atoms of angle	$2c_1^*$ Bond 1 ( $a_0$ )	$2c_2^*$ Bond 2 ( $a_0$ )	$2c_3^*$ Terminal Atom ( $a_0$ )	$E_{\text{terminal}}$ or $E$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2 (Eq. 15.14.4)	$C_1$	$C_2$	$c_1$	$c_2^*$	$E_T$ (eV)	$\theta_e$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle \text{H}_c \text{C}_a \text{H}_b$	2.09711	2.09711	3.4252	-15.75493	7	H		1	1	0.75	1.15796	0				109.50	
$\angle \text{H}_c \text{C}_a \text{O}_b$													70.56			109.44	110 (methyl nitrate)
$\angle \text{H}_c \text{C}_a \text{O}_b$	2.09711	2.71287	3.7238	-14.82575 $C_a$	1		0.83595 (Eq. 15.14.4)	0.75	1	0.75	0.93852	0				100.68	103 (methyl nitrate)
$\angle \text{O}_b \text{NO}_c$	2.27630	2.27630	4.1231	-16.68411 $O_a$	24		0.81549	1	1	1	0.81549	-1.44915				129.83	
$\angle \text{O}_b \text{NO}_c$														129.83		115.09 (Eq. 15.59.9)	118.1 (methyl nitrate)
$\angle \text{O}_b \text{NO}_c$														129.83		115.09 (Eq. 15.59.9)	112.4 (methyl nitrate)
$\angle \text{O}_b \text{NO}_c$	2.71287	2.65661	4.4721	-16.68412 $C_a$	25		0.81549	1	1	1	0.86345	-1.44915				112.79	112.7 (methyl nitrate)
$\angle \text{H}_c \text{C}_a \text{H}_b$	2.11106	2.11106	3.4252	-15.75493	7	H		1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle \text{C}_a \text{C}_b \text{C}_c$																	112 (propane)
$\angle \text{C}_a \text{C}_b \text{H}_c$													69.51			110.49	113.8 (butane)
$\angle \text{H}_c \text{C}_a \text{H}_b$	2.09711	2.09711	3.4252	-15.75493	7	H		1	1	0.75	1.15796	0				109.50	
$\angle \text{C}_a \text{C}_b \text{C}_c$													70.56			109.44	
$\angle \text{C}_a \text{C}_b \text{H}_c$													70.56			109.44	
$\angle \text{C}_a \text{C}_b \text{C}_c$	2.91547	2.91547	4.7958	-16.68412 $C_a$	25		0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle \text{C}_a \text{C}_b \text{H}_c$	2.91547	2.11323	4.1633	-15.55033 $C_a$	5		0.87495	0.75	1	0.75	1.04887	0				110.76	
$\angle \text{C}_a \text{C}_b \text{H}_c$	2.91347	2.09711	4.1633	-15.55033 $C_a$	5		0.87495	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle \text{C}_a \text{C}_b \text{C}_c$	2.90327	2.90327	4.7958	-15.55033 $C_a$	5		0.87495	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle \text{C}_a \text{C}_b \text{C}_c$													72.50			107.50	



## CYCLIC AND CONJUGATED ALKENES

$$(C_n H_{2n+2-2m-2c}, \quad n=3,4,5\ldots\infty, \quad m=1,2,3\ldots, \quad c=0 \text{ or } 1)$$

The cyclic and conjugated alkenes are represented by the general formula  $C_n H_{2n+2-2m-2c}$ ,  $n=3,4,5\ldots\infty$ ,  $m=1,2,3\ldots$ ,  $c=0$  or  $1$  where  $m$  is the number of double bonds and  $c=0$  for a straight-chain alkene and  $c=1$  for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, five distinct  $C-C$  functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 61A-E. In addition,  $CH_2$  of any  $-C=CH_2$  moiety is an conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group ( $CH_3$ ), and may comprise methylene ( $CH_2$ ), and methyne ( $CH$ ) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The  $C-C$  groups are solved in the same manner as those of the branched-chain alkanes given in the corresponding section. For example, the cyclopentene  $C_a-C_b$  group is equivalent to the  $n-C-C$  alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of  $H$  from the terminal methyl and methylene groups. Thus, the energy of each of the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene  $C_c-C_d$  and the cyclopentadiene  $C_a-C_b$  groups is the magnetic energy (Eq. (15.58)) which is subtracted from the  $C_a-C_b$  total bond energy according to Eqs. (13.524-13.527) due to the formation of a  $CH$  group from the methylene group.

$E_T(atom-atom,msp^3.AO)$  of the  $C=C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is equivalent to that of ethylene,  $-2.26759 \text{ eV}$ , given by



Eq. (14.247).  $E_r(\text{atom} - \text{atom}, msp^3.AO)$  of each  $C - C$ -bond MO in Eq. (15.52) is  $-2.26759 \text{ eV}$  or  $-1.85836 \text{ eV}$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of alkene,  $-1.13379 \text{ eV}$  (Eq. (14.247)), or methylene,  $-0.92918 \text{ eV}$  (Eq. (14.513)), groups, respectively, that are contiguous  
 5 with the  $C - C$ -bond carbons. In the former case, the total energy of the  $C - C$  bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of  $0.5e$  must be donated to the  $C - C$  bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the  $C - C$ -bond MO and increases the  $C - C$  bond energy. This additional lowering of the  $C - C$ -bond energy by additional charge  
 10 donation over that of an alkane bond due to adjacent double bonds is called *conjugation*.

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 61A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56))  
 15 parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum  
 20 of the  $E_D(\text{group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.79-15.108) are given in Table 15.212.



Table 15.207. The symbols of functional groups of cyclic and conjugated alkenes.

Functional Group	Group Symbol
CC double bond	C=C
1,3-butadiene, 1,3-pentadiene $C_s-C_s$	$C'-C' (a)$
1,3-cyclopentadiene $C_s-C_s$	$C'-C' (a)$
1,3-pentadiene $C_s-C_s$	$C'-C' (b)$
cyclopentene $C_s-C_s$	$C'-C' (b)$
1,4-pentadiene $C_s-C_s$	$C'-C' (c)$
1,3-cyclopentadiene $C_s-C_s$	$C'-C' (d)$
cyclopentene $C_s-C_s$	$C'-C' (e)$
CH <sub>2</sub> alkyl group	$C'-H (CH_2) (i)$
CH <sub>3</sub> group	$C'-H (CH_3)$
CH <sub>3</sub> alkyl group	$C'-H (CH_2) (ii)$
CH	$C'-H$

Table 15.208. The geometrical bond parameters of cyclic and conjugated alkenes and experimental values [1].

Parameter	C=C Group	$C'-C' (a)$ Group	$C'-C' (b)$ Group	$C'-C' (c)$ Group	$C'-C' (d)$ Group	$C'-C' (e)$ Group	$C-H (CH_2) (i)$ Group	$C-H (CH_2) (ii)$ Group	C-H Group
$a (a_e)$	1.47228	1.91256	2.04740	2.04740	2.04740	2.04740	1.64010	1.67122	1.67465
$c' (a_e)$	1.26661	1.38295	1.43087	1.43087	1.43087	1.43087	1.04566	1.05553	1.05661
Bond Length $2c' (A)$	1.34052	1.46365	1.51437	1.51437	1.51437	1.51437	1.10668	1.11713	1.11827
Exp. Bond Length $(A)$	1.349 (1,3-butadiene) 1.342 (1,3-cyclopentadiene) 1.342 (1,3-cyclopentadiene) 1.342 (cyclopentene)	1.467 (1,3-butadiene) 1.469 (1,3-cyclopentadiene)	1.519 (cyclopentene)	1.509 (1,3-cyclopentadiene)	1.546 (cyclopentene)	1.107 (2-methylpropane) 1.108 (avg.) 1.117 (1,3-butadiene)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.29569
$h, c (a_e)$	0.75055	1.32110	1.46439	1.46439	1.46439	1.46439	1.26354	1.27295	1.29924
$e$	0.86030	0.72309	0.69887	0.69887	0.69887	0.69887	0.63756	0.63159	0.63095



Table 15.209. The MO to HO intercept parameters of cyclic and conjugated alkenes  $R_1, R^*, R^*$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msy})^3 \text{AO}$ .

Bond	Atom	$E_b$ (eV) Bond 1	$E_b$ (eV) Bond 2	$E_b$ (eV) Bond 3	$E_b$ (eV) Bond 4	Final Total Energy ( $2sp^3$ ) (eV)	$r_{bond}$ ( $a_0$ )	$r_{bond}$ ( $a_0$ )	$E_{bond}(C2sp^3)$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C_2(H)C_2(H)C_2(H)$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.16	60.70	0.72040	0.54020
$H_1C_1=C_2(H)(H)C=C^R$ (1,3-butadiene, 1,3-pentadiene)	$C_2$	-1.13380	0	0	0	-152.74949	0.91771	0.85242	-15.95955	129.84	50.			



Table 15.210. The energy parameters (eV) of functional groups of cyclic and conjugated alkenes.

Parameters	C=C Group	C'-C' (a) Group	C'-C' (b) Group	C'-C' (c) Group	C'-C' (d) Group	C'-C' (e) Group	CH <sub>2</sub> (i) Group	CH <sub>3</sub> Group	CH <sub>2</sub> (ii) Group	C-H Group
$\eta_1$	2	1	1	1	1	1	2	3	2	1
$\eta_2$	0	0	0	0	0	0	1	2	1	0
$\eta_3$	0	0	0	0	0	0	0	0	0	0
$\zeta_1$	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75
$\zeta_2$	0.91771	1	1	1	1	1	1	1	1	1
$\zeta_3$	1	1	1	1	1	1	1	1	1	1
$\zeta_4$	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
$\zeta_5$	0	0	0	0	0	0	1	0	1	1
$\zeta_6$	4	2	2	2	2	2	1	1	1	1
$\zeta_7$	0	0	0	0	0	0	2	3	2	1
$\zeta_8$	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75
$\zeta_9$	0.91771	1	1	1	1	1	1	1	1	1
$\zeta_{10}$	-102.08992	-33.01226	-30.19634	-30.19634	-30.19634	-28.79214	-72.03287	-107.32728	-70.41425	-35.12015
$V_e$ (eV)	21.48386	9.83824	9.50874	9.50874	9.50874	9.33352	26.02344	38.92728	25.78002	12.87680
$V_p$ (eV)	34.67062	8.63041	7.37432	7.37432	7.37432	6.77464	21.95990	32.53914	21.06675	10.48582
$V_m$ (eV)	-17.33551	-4.31520	-3.68716	-3.68716	-3.68716	-3.38732	-10.97995	-16.26957	-10.53337	-5.24291
$E_{1,100}$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
$\Delta E_{1,100}$ (eV)	0	-1.85836	0	0	0	0	0	0	0	0
$E_p$ (eV)	0	-12.77653	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
$E_p$ (eV)	-63.27075	-31.63535	-31.63534	-31.63534	-31.63534	-31.63537	-49.66437	-67.69451	-49.66493	-31.63533
$E_p$ (eV)	-2.26759	-2.26759	-1.85836	-1.85836	-1.85836	-1.85836	0	0	0	0
$E_p$ (eV)	-65.53833	-33.90295	-33.49373	-33.49373	-33.49373	-33.49373	-49.66493	-67.69450	-49.66493	-31.63537
$\omega$ (10 <sup>6</sup> rad/s)	43.0680	11.0522	9.97851	23.3291	9.97851	9.43699	25.2077	24.9286	24.2751	24.1759
$E_k$ (eV)	28.34813	7.27475	6.56803	15.35563	6.56803	6.21159	16.59214	16.40846	15.97831	15.91299
$\bar{E}_D$ (eV)	-0.34517	-0.18090	-0.16982	-0.25966	-0.16982	-0.16515	-0.25493	-0.25352	-0.25017	-0.24966
$\bar{E}_{D,100}$ (eV)	0.17897	0.14829	0.11159	0.11159	0.11159	0.12312	0.35532	0.35532	0.35532	0.35532
$\bar{E}_{D,100}$ (eV)	-0.25568	-0.10676	-0.11402	-0.20386	-0.11402	-0.10359	-0.07727	-0.22757	-0.14502	-0.07200
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_p$ (eV)	-66.04969	-34.00972	-33.60776	-33.69760	-33.60776	-33.59732	-49.81948	-67.92207	-49.80996	-31.70737
$E_{mag}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{mag}$ (eV)	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844
$E_p$ (eV)	7.51014	4.73994	4.33798	4.42782	4.18995	4.32754	7.83968	12.49186	7.83016	3.32601

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the 5 weighted sum of the  $E_{p,i(mag)}$  (eV) values based on composition is given by (15.58).

Formula	Name	C=C	C'-C' (a)	C'-C' (b)	C'-C' (c)	C'-C' (d)	C'-C' (e)	CH	CH <sub>2</sub> (i)	CH <sub>3</sub>	CH <sub>2</sub> (ii)	CH	$E_{mag}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>4</sub> H <sub>6</sub>	1,3 Butadiene	2	1	0	0	0	0	2	0	0	0	2	0	42.12705	42.12705	0.00084
C <sub>4</sub> H <sub>6</sub>	1,3 Pentadiene	2	1	1	0	0	0	0	0	1	0	0	0	54.42484	54.42484	0.00031
C <sub>4</sub> H <sub>6</sub>	1,4 Pentadiene	2	0	0	2	0	0	2	0	0	1	2	0	54.03745	54.11866	0.00149
C <sub>5</sub> H <sub>8</sub>	1,3 Cyclopentadiene	2	1	0	0	2	0	1	0	0	1	4	0	49.27432	49.30294	0.00058
C <sub>5</sub> H <sub>8</sub>	Cyclopentene	1	0	2	0	0	0	2	3	0	2	2	-1	54.83565	54.86117	0.00047



Table 15.2.12. The bond angle parameters of cyclic and conjugated alkenes and experimental values [1]. In the calculation of  $\theta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(atom - atom, msp, AO)$ .

Atoms of Angle	$2c_1$ Bond 1 ( $a_0$ )	$2c_2$ Bond 2 ( $a_0$ )	$2c_3$ Terminal Atom ( $a_0$ )	$E_{r,terminal}$ Atom 1 (Table 15.3.A)	Atom 1 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c'_1$	$E_r$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle HC_1H$ $H_1C_1 = C_h$ 1,3-butadiene	2.09132	2.09132	3.4928	-15.95955	9	0.85252	1	1	1	0.75	1.17300	0				113.25	
$\angle C_1C_2H_u$ $H_1C_1 = C_h$ 1,3-butadiene														113.25		123.38	120.9 (1,3-butadiene)
$\angle C_1C_2H_u$ $H_1C_1 = C_h$ 1,3-butadiene	2.53321	2.09132	4.0000	-15.95954	9	0.85252	0.85252	0.75	1	0.75	1.00000	0				119.45	120.9 (1,3-butadiene)
$\angle C_1C_2C_h$ $C_h = C'_h$ 1,3-butadiene	2.53321	2.76590	4.6904	-16.88873	27	0.80561	0.79597	1	1	1	0.85395	-1.85336				124.48	124.4 (1,3-butadiene CCC) 124.4 (1,3,5-hexatriene C6CCcC) 121.7 (1,3,5-hexatriene C6C6Cc) 125.3 (2-butene C6C6Cc)
$\angle C_1C_2C'_h$ $C_h = C'_h$ 1,3-cyclopentadiene	2.53321	2.76590	4.3012	-17.81791	46	0.76360	0.76360	1	1	1	0.76360	-1.85336				108.44	109.4 (1,3-cyclopentadiene)
$\angle C_1C_2C'_h$ $C_h = C'_h$ 1,3-cyclopentadiene	2.86175	2.53321	4.3818	-17.61330	42	0.77247	0.77247	1	1	1	0.77247	-1.85336				108.47	109.3 (1,3-cyclopentadiene)
$\angle C_1C_2C_h$ $= C_h, HC_1H_2(H) =$ 1,3-cyclopentadiene	2.86175	2.86175	4.4609	-17.40869	38	0.78155	0.78155	1	1	1	0.78155	-1.85336				102.41	102.8 (1,3-cyclopentadiene)
$\angle C_1C_2C'_h$ $-H_1C_1, HC_1 = C_h, HC_1H_2 -$ cyclopentene	2.86175	2.53321	4.4272	-17.61330	42	0.78155	0.77247	1	1	1	0.77701	-1.85336				110.14	110.0 (cyclopentene)
$\angle C_1C_2C'_h$ $-H_1C_1, HC_1, HC_1 = C_h, H -$ cyclopentene	2.91548	2.86175	4.5166	-17.20408	35	0.79085	0.78155	1	1	1	0.78620	-1.85336				102.85	103.0 (cyclopentene)
$\angle C_1C_2C_h$ $-C_h, HC_1, HC_1H_2 -$ cyclopentene	2.91548	2.91548	4.5826	-17.20408	35	0.79085	0.79085	1	1	1	0.79085	-1.85336				103.61	104.0 (cyclopentene)



## AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple  $H_2$ -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule ( $C_6H_6$ ) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

$C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a  $C-H$  bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a  $C=C$  bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule ( $CH_2CH_2$ ) section. The radius  $r_{ethylene, 2sp^3}$  ( $0.85252a_0$ ) of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  ( $-15.95955 eV$ ) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  ( $-15.76868 eV$ ) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.246).  $E_T(C=C, 2sp^3)$  ( $-1.13380 eV$ ) (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the  $C=C$ -bond MO is given by the difference between  $E(C_{ethylene}, 2sp^3)$  and  $E(C, 2sp^3)$ .  $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each  $2sp^3$  HO of each carbon atom initially has four unpaired electrons. Thus, the 6  $H$  atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon atoms contribute twenty-four electrons to form six  $C-H$  bonds and six  $C=C$  bonds. Each  $C-H$  bond has two paired electrons with one donated from the  $H$  AO and the other from the  $C2sp^3$  HO. Each  $C=C$  bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each  $C-H$  and each  $C=C$  bond comprises a linear combination



of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of  $C = C$ -bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds  
5 comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$\left( \begin{array}{l} 3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C \overset{4e}{=} C) - \text{ethylene-type-bond MO} \\ \rightarrow 6(C \overset{3e}{=} C) - \text{bond MO of benzene} \end{array} \right) \quad (15.142)$$

10 The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the  $C = C$ -bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond  $C = C$ -bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the  $C = C$ -bond MO of ethylene (Eqs. (14.242-  
15 14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each  $C = C$ -bond gives rise to the  $C_{benzene} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C_{benzene}, 2sp^3)$  given by Eq. (14.245). To meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $C_2$  of Eq. (15.42) for the aromatic  $C \overset{3e}{=} C$ -bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  
20  $E_{Coulomb}(C_{benzene}, 2sp^3)$  (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  (Eq. (1.243)):

$$C_2(benzene C2sp^3 HO) = c_2(benzene C2sp^3 HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252 \quad (15.143)$$

The energies of each  $C \overset{3e}{=} C$  bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of  
25 benzene. Ethylene serves as a basis element for the  $C \overset{3e}{=} C$  bonding of benzene wherein each of the six  $C \overset{3e}{=} C$  bonds of benzene comprises  $(0.75)(4) = 3$  electrons according to Eq. (15.142).



The total energy of the bonds of the eighteen electrons of the  $C \equiv C^{3e}$  bonds of benzene,  $E_T(C_6H_6, C \equiv C^{3e})$ , is given by (6)(0.75) times  $E_{T+osc}(C = C)$  (Eq. (14.492)), the total energy of the  $C \equiv C^{3e}$ -bond MO of benzene including the Doppler term, minus eighteen times  $E(C, 2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each  $C$  that forms the  $C \equiv C^{3e}$  bonds of bond order two. Thus, the total energy of the six  $C \equiv C^{3e}$  bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned} E_T(C_6H_6, C \equiv C^{3e}) &= (6)(0.75)E_{T+osc}(C = C) - (6)(3)E(C, 2sp^3) \\ &= (6)(0.75)(-66.05796 \text{ eV}) - 18(-14.63489 \text{ eV}) \\ &= -297.26081 \text{ eV} - (-263.42798 \text{ eV}) \\ &= -33.83284 \text{ eV} \end{aligned} \quad (15.144)$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.

$E_{hv}$  of an aromatic bond is given by  $E_T(H_2)$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_2$ -type MO such that

$$\bar{E}_{osc} = n_1(\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left( -31.63536831 \text{ eV} \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (15.145)$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule ( $C_6H_6$ ) section modifies Eqs. (15.52-15.56). Multiplication of the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the

total energy of the aromatic bond:

$$E_T(\text{Group}) = f_1 \left( \begin{aligned} &E(\text{basis energies}) + E_T(\text{atom-atom, } msp^3 \text{ AO}) \\ &-31.63536831 \text{ eV} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\epsilon_o R^3}}}{m_e c^2} + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3}} \end{aligned} \right) \quad (15.146)$$



The total bond energy of the aromatic group  $E_D(\text{Group})$  is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of  $c_4 E_{\text{initial}}(c_4 \text{ AO} / \text{HO})$  and  $c_5 E_{\text{initial}}(c_5 \text{ AO} / \text{HO})$ :

$$E_D(\text{Group}) = - \left[ f_1 \left( \begin{aligned} & E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) \\ & - 31.63536831 \text{ eV} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_o R^3}}}{m_e}} + n_1 \bar{E}_{\text{Kvib}} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \end{aligned} \right) - (c_4 E_{\text{initial}}(\text{AO} / \text{HO}) + c_5 E_{\text{initial}}(c_5 \text{ AO} / \text{HO})) \right] \quad (15.147)$$

5 Since there are three electrons per aromatic bond,  $c_4$  is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six  $\text{CH}$  radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of  $\text{CH}$  is given in the Hydrogen Carbide ( $\text{CH}$ ) section. Those of the  
10 benzene are given in the Benzene Molecule ( $\text{C}_6\text{H}_6$ ) section. The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that  $E_T(C = C, 2sp^3) = -1.13379 \text{ eV}$  (Eq. (14.247)) is subtracted from  $E_T(\text{CH})$  of Eq. (13.495) to match the energy of each  $\text{C}-\text{H}$ -bond MO to the decrease in the energy of the corresponding  $\text{C}2sp^3$  HO. In the corresponding generalization of the aromatic  $\text{CH}$  group, the geometrical  
15 parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) = -1.13379 \text{ eV}$ .

The total energy of the benzene  $\text{C}-\text{H}$ -bond MO,  $E_{T_{\text{benzene}}}(C-H)$ , given by Eq. (14.467) is the sum of  $0.5E_T(C = C, 2sp^3)$ , the energy change of each  $\text{C}2sp^3$  shell per single bond due to the decrease in radius with the formation of the corresponding  $\text{C}=\text{C}$ -bond MO (Eq. (14.247)),  
20 and  $E_{T_{\text{benzene}}}(\text{CH})$ , the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic  $\text{CH}$  group, the energy parameters are determined using Eqs. (15.146-15.147) with  $f_1 = 1$  and  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) = \frac{-1.13379 \text{ eV}}{2}$ . Thus, the energy



contribution to the single aromatic  $CH$  bond is one half that of the  $C=C$  double bond contribution. This matches the energies of the  $CH$  and  $C=C$  aromatic groups, conserves the electron number with the equivalent charge density as that of  $s=1$  in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic  $C=C$  bonds to give  $CH$  groups creates unpaired electrons in these fragments that corresponds to  $c_3=1$  in Eq. (15.56) with  $E_{mag}$  given by Eq. (15.58).

Each of the  $C-H$  bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each  $C-H$  bond,  $-E_{D_{benzene}}(^{12}CH)$  (Eq. (14.477)), the total energy of the twelve electrons of the six  $C-H$  bonds of benzene,  $E_T(C_6H_6, C-H)$ , given by Eq. (14.494) is

$$E_T(C_6H_6, C-H) = (6) \left( -E_{D_{benzene}}(^{12}CH) \right) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV} \quad (15.148)$$

The total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , given by Eq. (14.495) is the negative sum of  $E_T(C_6H_6, C=C)$  (Eq. (14.493)) and  $E_T(C_6H_6, C-H)$  (Eq. (14.494)):

$$\begin{aligned} E_D(C_6H_6) &= - \left( E_T(C_6H_6, C=C) + E_T(C_6H_6, C-H) \right) \\ &= - \left( (-33.83284 \text{ eV}) + (-23.42724 \text{ eV}) \right) \\ &= 57.2601 \text{ eV} \end{aligned} \quad (15.149)$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule ( $C_6H_6$ ) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.



Table 15.213. The symbols of functional groups of aromatics and heterocyclics.

Functional Group	Group Symbol
CC (aromatic bond)	$\text{C}^{\text{ar}}$
CH (aromatic)	$\text{CH}(\text{I})$

Table 15.214. The geometrical bond parameters of aromatics and heterocyclics and experimental values [1].

Parameter	$\text{C}^{\text{ar}}$ Group	CH Group
$a$ ( $a_0$ )	1.47348	1.60061
$c'$ ( $a_0$ )	1.31468	1.03299
Bond Length $2c'$ ( $\text{\AA}$ )	1.39140	1.09327
Exp. Bond Length ( $\text{\AA}$ )	1.399 (benzene)	1.101 (benzene)
$h, c$ ( $a_0$ )	0.66540	1.22265
$e$	0.89223	0.64537

5 Table 15.215. The MO to HO intercept geometrical bond parameters of benzene.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{exp}^2, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $\text{C}^{\text{ar}}$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{total}}(\text{C}^{\text{ar}})$ (eV) Final	$\bar{E}(\text{C}^{\text{ar}})$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$\text{C}^{\text{ar}} - \text{H}(\text{CH})$	C	-0.85035	-0.85035	-0.85035	0	-153.88327	0.91771	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\text{C}^{\text{ar}} = \text{H}(\text{C}^{\text{ar}} = \text{C})$	C <sub>u</sub>	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533



Table 15.216. The energy parameters (eV) of functional groups of aromatics and hertocyclics.

Parameters	<sup>3s</sup> C=C Group	CH Group
$f_1$	0.75	1
$n_1$	2	1
$n_2$	0	0
$n_3$	0	0
$C_1$	0.5	0.75
$C_2$	0.85252	1
$c_1$	1	1
$c_2$	0.85252	0.91771
$c_3$	0	1
$c_4$	3	1
$c_5$	0	1
$C_{1o}$	0.5	0.75
$C_{2o}$	0.85252	1
$V_u$ (eV)	-101.12679	-37.10024
$V_p$ (eV)	20.69825	13.17125
$T$ (eV)	34.31559	11.58941
$V_m$ (eV)	-17.15779	-5.79470
$E_{(AOIHO)}$ (eV)	0	-14.63489
$\Delta E_{H_2MO(AOIHO)}$ (eV)	0	-1.13379
$E_T(AOIHO)$ (eV)	0	-13.50110
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539
$E_T(atom - atom, msp^3.AO)$ (eV)	-2.26759	-0.56690
$E_T(MO)$ (eV)	-65.53833	-32.20226
$\omega$ ( $10^{15}$ rad / s)	49.7272	26.4826
$E_K$ (eV)	32.73133	17.43132
$\bar{E}_D$ (eV)	-0.35806	-0.26130
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364
$E_{mag}$ (eV)	0.14803	0.14803
$E_T(Group)$ (eV)	-49.54347	-32.28590
$E_{initial}(c_4 AOIHO)$ (eV)	-14.63489	-14.63489
$E_{initial}(c_5 AOIHO)$ (eV)	0	-13.59844
$E_D(Group)$ (eV)	5.63881	3.90454



Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Formula	Name	$\sum C=C$	$\sum C-H$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_6$	Benzene	6	6	57.26008	57.26340	0.00006

Table 15.218. The bond angle parameters of benzene and experimental values [1].  $E_T$  is  $E_T(atom - atom, msp^2, AO)$ .

Atoms of Angle	$2c_1'$ Bond 1 ( $\sigma_g$ )	$2c_2'$ Bond 2 ( $\sigma_g$ )	$2c_1'$ Terminal Atoms ( $\sigma_g$ )	$E_{\text{terminal-Atom 1}}$	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{terminal-Atom 2}}$	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c_2'$	$E_T$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle(C-C)$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.55536				120.19	120 [50-52] (benzene)
$\angle(C-H)$ (aromatic)																120.19		119.91	120 [50-52] (benzene)



## NAPHTHALENE

Naphthalene has the formula  $C_{10}H_8$  and comprises a planar molecule with two aromatic rings that share a common  $C-C$  group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is  
 5  $(0.75)(4) = 3$  as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a  $C-C$  single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging  $C-C$  single bond, and 16 electrons form the eight  $C-H$  single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.42), (15.1-15.5), and  
 10 (15.146-15.147)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond,  $c_4$  is three times ten, the number of aromatic bonds. Similarly, the aromatic  $C-H$  group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten  $C2sp^3$  HOs bridged by the  $C-C$  single bond, the parameters  $c_1$ ,  $C_2$ , and  $C_{2o}$  of Eq. (15.42) are one for the  $C-C$  group,  
 15  $C_{1o}$  and  $C_1$  are 0.5, and  $c_2$  given by Eq. (15.142) is  $c_2(C2sp^3HO) = 0.85252$ . Otherwise, the solutions of the  $C-C$  bond parameters are equivalent to those of the replaced  $C-H$  groups with  $E(AO/HO) = -14.63489 \text{ eV}$  and  $\Delta E_{H_2MO}(AO/HO) = -1.13379 \text{ eV}$  in Eq. (15.41). Similarly, the energy parameters are determined using Eqs. (15.52-15.56) with  

$$E_T(atom - atom, msp^3.AO) = \frac{-1.13379 \text{ eV}}{2}.$$

20 The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 62. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum  
 25 over the integer multiple of each  $E_D(\text{Group})$  of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.79-15.108) are given in Table 15.224.



Table 15.219. The symbols of functional groups of naphthalene.

Functional Group	Group Symbol
C=C (aromatic bond)	C=C
CH (aromatic)	CH (i)
C <sub>sp</sub> -C <sub>sp</sub> (bridging bond)	C-C

Table 15.220. The geometrical bond parameters of naphthalene and experimental values [1].

Parameter	C=C Group	CH Group	C-C Group
$\sigma$ (Å)	1.47348	1.60661	1.75607
$\sigma'$ (Å)	1.31468	1.03299	1.32517
Bond Length $2c'$ (Å)	1.39140	1.09327	1.40250
Exp. Bond Length (Å)	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)
$h_{\sigma}c'$ (Å)	0.66540	1.22265	1.15226
$\sigma$	0.89223	0.64537	0.75462

Table 15.221. The MO to H0 intercept geometrical bond parameters of naphthalene.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy C2sp <sup>3</sup> (eV)	$r_{\text{final}}$ (Å)	$E_{\text{total}}$ (C2sp <sup>3</sup> ) (eV) Final	$E$ (C2sp <sup>3</sup> ) (eV) Final	$\theta$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (Å)	$d_2$ (Å)
C-H (CH)	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
C=HC=C	C <sub>sp</sub>	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
C=C <sub>sp</sub> (C <sub>sp</sub> )=C	C <sub>sp</sub>	-0.85035	-0.85035	-0.38345	0	-153.59983	0.91771	-16.80989	-16.61903	134.81	45.19	59.66	0.74439	0.57038
(C <sub>sp</sub> ) <sub>2</sub> C <sub>sp</sub> -C <sub>sp</sub> (C <sub>sp</sub> ) <sub>2</sub>	C <sub>sp</sub>	-0.85035	-0.85035	-0.38345	0	-153.59983	0.91771	-16.80989	-16.61903	99.50	80.50	47.66	1.18269	0.14248



Table 15.222. The energy parameters (eV) of functional groups of naphthalene.

Parameters	$\overset{3e}{C=C}$ Group	CH Group	C - C Group
$f_1$	0.75	1	1
$n_1$	2	1	1
$n_2$	0	0	0
$n_3$	0	0	0
$C_1$	0.5	0.75	0.5
$C_2$	0.85252	1	1
$c_1$	1	1	1
$c_2$	0.85252	0.91771	0.85252
$c_3$	0	1	0
$c_4$	3	1	2
$c_5$	0	1	0
$C_{1o}$	0.5	0.75	0.5
$C_{2o}$	0.85252	1	1
$V_e$ (eV)	-101.12679	-37.10024	-34.43791
$V_p$ (eV)	20.69825	13.17125	10.26723
$T$ (eV)	34.31559	11.58941	9.80539
$V_m$ (eV)	-17.15779	-5.79470	-4.90270
$E_{AOIHO}$ (eV)	0	-14.63489	-14.63489
$\Delta E_{H_2MO(AOIHO)}$ (eV)	0	-1.13379	-1.13379
$E_T(AOIHO)$ (eV)	0	-13.50110	-13.50110
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63529
$E_T(atom - atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.56690
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.20226
$\omega$ ( $10^{15}$ rad / s)	49.7272	26.4826	23.6343
$E_K$ (eV)	32.73133	17.43132	15.55648
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.25127
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.18971
$E_{mag}$ (eV)	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-49.54347	-32.28590	-32.39198
$E_{initial}(c_1 AOIHO)$ (eV)	-14.63489	-14.63489	-14.63489
$E_{initial}(c_3 AOIHO)$ (eV)	0	-13.59844	0
$E_D(Group)$ (eV)	5.63881	3.90454	3.12220



Table 15.223. The total bond energies of naphthalene calculated using the functional group composition and the energies of Table 15.222 compared to the experimental values [2].

Formula	Name	C=C	C <sup>+</sup>	C <sup>-</sup>	C-C	C <sup>+</sup>	C <sup>-</sup>	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>10</sub> H <sub>8</sub>	Naphthalene	10	8	1	1			90.74658	90.79143	0.00049

Table 15.224. The bond angle parameters of naphthalene and experimental values [1].  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Atoms of Angle	2C <sup>+</sup> Bond 1 (a <sub>1</sub> )	2C <sup>+</sup> Bond 2 (a <sub>2</sub> )	2C <sup>+</sup> Terminal Atoms (a <sub>3</sub> )	$E_{\text{calculated}}^T$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{\text{calculated}}^T$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	C <sub>2</sub> Atom 1	C <sub>2</sub> Atom 2	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	$\phi_1$	$\phi_2$	$\phi_3$	$\phi_4$	$E_T$ (eV)	$\theta_1$ (°)	$\theta_2$ (°)	Cal. $\theta$ (°)	Exp. $\theta$ (°)
$\angle C_1 C_2 C_3$ (naphthalene)	2.62936	2.65034	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	1					-1.85836			119.40	119.4 (naphthalene)
$\angle C_2 C_3 H$ (naphthalene)															119.40						120.30	
$\angle C_1 C_2 C_3$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	1					-1.85836			120.19	120 [50-52] (benzene)
$\angle C_2 C_3 H$ (aromatic)															120.19						119.91	120 [50-52] (benzene)



## TOLUENE

Toluene has the formula  $C_7H_8$  and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a  $CH_3$  functional group and a  $C-C$  functional group. The aromatic  $C=C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $CH_3$  functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a  $C-C$  functional group that is are solved using the same principles as those used to solve the alkane functional groups wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons,  $E(AO/HO)$  and  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.41) are  $-15.35946 \text{ eV}$  (Eq. (14.155)) and  $\frac{-1.13379 \text{ eV}}{2}$ , respectively.

To meet the equipotential condition of the union of the aromatic and methyl  $C2sp^3$  HOs of the  $C-C$  single bond, the parameters  $c_1$ ,  $C_2$ , and  $C_{2o}$  of Eq. (15.42) are one for the  $C-C$  group,  $C_{1o}$  and  $C_1$  are 0.5, and  $c_2$  given by Eq. (13.430) is  $c_2(C2sp^3HO) = 0.91771$ . To match the energies of the functional groups,  $E_T(atom - atom, msp^3.AO)$  of the  $C-C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is  $-1.13379 \text{ eV}$  which is the same energy per  $C2sp^3$  HO as that of the replaced  $C-H$  group.

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.79-15.108) are given in Table 15.230.



Table 15.225. The symbols of functional groups of toluene.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{\text{ar}}{\text{C}}-\text{C}$
CH (aromatic)	$\text{C}(\text{H})$
$\text{C}'-\text{C}'$ ( $\text{CH}_3$ to aromatic bond)	$\text{C}'-\text{C}'$
$\text{CH}_3$ group	$\text{C}-\text{H}(\text{CH}_3)$

Table 15.226. The geometrical bond parameters of toluene and experimental values [1].

Parameter	$\overset{\text{ar}}{\text{C}}=\text{C}$ Group	CH (i) Group	$\text{C}'-\text{C}'$ Group	$\text{C}-\text{H}(\text{CH}_3)$ Group
$a$ ( $a_0$ )	1.47348	1.60061	2.06004	1.64920
$c'$ ( $a_0$ )	1.31468	1.03299	1.43528	1.04856
Bond Length				
$2c'$ ( $\text{\AA}$ )	1.39140	1.09327	1.51904	1.10974
Exp. Bond Length	1.399 (toluene)	1.11 (avg.) (toluene)	1.524 (toluene)	1.11 (avg.) (toluene)
$h_2c'$ ( $a_0$ )	0.66340	1.22265	1.47774	1.27295
$e$	0.89223	0.64537	0.69673	0.63580

Table 15.227. The MO to HO intercept geometrical bond parameters of toluene.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{resp. AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy C2sp <sup>3</sup> (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{total}}(\text{C2sp}^3)$ (eV) Final	$E(\text{C2sp}^3)$ (eV) Final	$\theta^\circ$	$\theta_1^\circ$	$\theta_2^\circ$	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$\text{C}-\text{H}(\text{CH}_3)$	$\text{C}_a$	-0.56690	0	0	0	-152.18259	0.91771	-15.39265	-15.20178	79.89	101.11	43.13	1.20367	0.15311
$\text{C}-\text{H}(\text{CH}_3)$	$\text{C}_c$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\text{C}'=\text{H}_a=\text{C}$	$\text{C}_c$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\text{C}'=\text{H}_c(\text{H}_c)\text{C}_a=\text{C}$	$\text{C}_c$	-0.85035	-0.85035	-0.56690	0	-152.18259	0.91771	-15.39265	-15.20178	73.38	106.62	34.97	1.68807	0.25279
$\left(\text{C}'=\text{H}_c\right)_2\text{C}_a-\text{C}_c\text{H}_3$	$\text{C}_c$	-0.56690	0	0	0	-152.18259	0.91771	-17.09334	-16.90247	61.56	118.44	28.27	1.81430	0.37901
$\left(\text{C}'=\text{H}_c\right)_2\text{C}_a-\text{C}_c\text{H}_3$	$\text{C}_c$	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	-17.09334	-16.90247					



Table 15.228. The energy parameters (eV) of functional groups of toluene.

Parameters	${}^3\sigma$ $C=C$ Group	$CH$ (i) Group	$C-C$ Group	$CH_3$ Group
$f_1$	0.75	1		
$n_1$	2	1	1	3
$n_2$	0	0	0	2
$n_3$	0	0	0	0
$C_1$	0.5	0.75	0.5	0.75
$C_2$	0.85252	1	1	1
$c_1$	1	1	1	1
$c_2$	0.85252	0.91771	0.91771	0.91771
$c_3$	0	1	0	0
$c_4$	3	1	2	1
$c_5$	0	1	0	3
$C_{1o}$	0.5	0.75	0.5	0.75
$C_{2o}$	0.85252	1	1	1
$V_v$ (eV)	-101.12679	-37.10024	-29.95792	-107.32728
$V_p$ (eV)	20.69825	13.17125	9.47952	38.92728
$T$ (eV)	34.31559	11.58941	7.27120	32.53914
$V_m$ (eV)	-17.15779	-5.79470	-3.63560	-16.26957
$E_{AO/HO}$ (eV)	0	-14.63489	-15.35946	-15.56407
$\Delta E_{H_2MO(AO/HO)}$ (eV)	0	-1.13379	-0.56690	0
$E_T(AO/HO)$ (eV)	0	-13.50110	-14.79257	-15.56407
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63537	-67.69451
$E_T(atom-atom,msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	0
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.76916	-67.69450
$\omega$ ( $10^{15}$ rad / s)	49.7272	26.4826	16.2731	24.9286
$E_K$ (eV)	32.73133	17.43132	10.71127	16.40846
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.21217	-0.25352
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.14940 [53]	0.35532 (Eq. (13.458))
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.13747	-0.22757
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-49.54347	-32.28590	-32.90663	-67.92207
$E_{initial}(c_1 AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5 AO/HO)$ (eV)	0	-13.59844	0	-13.59844
$E_D(Group)$ (eV)	5.63881	3.90454	3.63685	12.49186



Table 15.229. The total bond energies of toluene calculated using the functional group composition and the energies of Table 15.228 compared to the experimental values [2].

Formula	Name	$C=C$	$C-H$ (i)	$C-H$ Group	$C-H_3$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_6$	Toluene	6	5	1	1	69.546	69.546	0.00088

Table 15.230. The bond angle parameters of toluene and experimental values [1].  $E_T$  is  $E_T(atom-atom,exp, AO)$ .

Atoms of Angle	$2c'$ Bond 1 ( $a_0$ )	$2c'$ Bond 2 ( $a_0$ )	$2c'$ Terminal Atoms ( $a_0$ )	$E_{T,calc}$ Atom 1	$E_{T,calc}$ Atom 2	Atom 1 Hybridization Designation (Table 15.3.A)	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c_2'$	$E_T$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C'CC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	-17.17218	34	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle C'CH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)



## CHLOROBENZENES

Chlorobenzenes have the formula  $C_6H_{6-m}Cl_m$  and comprise the benzene molecule with at least one hydrogen atom replaced by a chlorine atom corresponding to a  $C-Cl$  functional group. The aromatic  $C \equiv C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to  $E_{osc}$ . Two types of  $C-Cl$  functional groups can be identified based on symmetry that determine the parameter  $R$  in Eq. (15.48). One corresponds to the special case of 1,3,5 substitution and the other corresponds to other cases of single or multiple substitutions of  $Cl$  for  $H$ . P-dichlorobenzene is representative of the bonding with  $R = a$ . 1,2,3-trichlorobenzene is the particular case wherein is  $R = b$ . Also, beyond the binding of three chlorides  $E_{mag}$  is subtracted for each additional  $Cl$  due to the formation of an unpaired electrons on each  $C-Cl$  bond.

The bond between the chlorine and aromatic ring comprises two  $C-Cl$  functional groups that are solved using the same principles as those used to solve the alkyl chloride functional groups as given in the corresponding section wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and  $Cl$  AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. As in the case of alkyl chlorides,  $c_2$  of Eq. (15.52) for each  $C-Cl$ -bond MO is one, and the energy matching condition is determined by the  $C_2$  parameter given by Eq. (15.111) which is  $C_2(C2sp^3HO \text{ to } Cl) = 0.81317$ . To match energies within the MO that bridges the chlorine AO and aromatic carbon  $C2sp^3$  HO,  $E(AO / HO)$  and  $\Delta E_{H_2MO}(AO / HO)$  in Eq. (15.42) are  $-14.63489 \text{ eV}$  and  $-2.99216 \text{ eV}$ , respectively. The latter matches twice that of the replaced  $C-H$ -bond MO plus  $E_T(atom - atom, msp^3.AO)$ . To match the energies of the functional groups,  $E_T(atom - atom, msp^3.AO)$  of the  $C-Cl$ -bond MO in Eq. (15.53) due to the charge donation from the  $C$  and  $Cl$  atoms to the MO is  $-0.72457 \text{ eV}$  (Eq. (14.151)).



The symbols of the functional groups of chlorobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of chlorobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each chlorobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of chlorobenzenes determined using Eqs. (15.79-15.108) are given in Table 15.236.

Table 15.231. The symbols of functional groups of chlorobenzenes.

Functional Group	Group Symbol
CC (aromatic bond)	$C \overset{3e}{=} C$
CH (aromatic)	CH (i)
Cl - C (Cl to aromatic bond)	C - Cl (a)
Cl - C (Cl to aromatic bond of 1,3,5-trichlorobenzene)	C - Cl (b)



Table 15.23.2. The geometrical bond parameters of chlorobenzenes and experimental values [1].

Parameter	$\text{C}=\text{C}$ Group	$\text{C}-\text{H}$ (l) Group	$\text{C}-\text{Cl}$ (a) Group	$\text{C}-\text{Cl}$ (b) Group
$a$ ( $a_0$ )	1.47348	1.60061	2.20799	2.20799
$c'$ ( $a_0$ )	1.31468	1.03299	1.64782	1.64782
Bond Length $2c'$ ( $\text{\AA}$ )	1.39140	1.09327	1.74397	1.74397
Exp. Bond Length ( $\text{\AA}$ )	1.400 (chlorobenzene)	1.083 (chlorobenzene)	1.737 (chlorobenzene)	1.737 (chlorobenzene)
$h, c$ ( $a_0$ )	0.66540	1.2265	1.46967	1.46967
$e$	0.89223	0.64537	0.74630	0.74630

Table 15.23.3. The MO to HO intercept geometrical bond parameters of chlorobenzenes.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy ( $2, sp^3$ ) (eV)	$r_{\text{bond}}$ ( $a_0$ )	$r_{\text{bond}}$ ( $a_0$ )	$E_{\text{bond}}(2, sp^3)$ (eV) Final	$E(C2, sp^3)$ (eV) Final	$\theta^1$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$\text{C}-\text{H}(\text{C}, \text{H})$	$\text{C}_\text{H}$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.59248	74.42	105.58	38.84	1.24678	0.21379
$\text{C}=\text{HC}_\text{H}=\text{C}$	$\text{C}_\text{H}$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.59248	134.24	45.76	58.98	0.75935	0.55533
$\text{C}=\text{C}_\text{H}-\text{Cl}$	$\text{C}_\text{H}$	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	73.32	106.68	31.67	1.87911	0.23129
$\text{C}=\text{C}_\text{H}-\text{Cl}$	$\text{Cl}$	-0.36229	0	0	0		1.05158	0.89582	15.18804		82.92	97.08	37.22	1.75824	0.11042
$\text{C}_\text{H}=\text{C}(\text{Cl})\text{C}_\text{H}=\text{C}_\text{H}$ ( $\text{C}_\text{H}$ bound to $\text{H}$ or $\text{Cl}$ )	$\text{C}_\text{H}$	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45.35	59.47	0.74854	0.56614



TABLE 10-10: The energy parameters (eV) of functional groups of chlorobenzenes.

Parameters	$\overset{\text{ar}}{C=C}$ Group	CH (i) Group	C-Cl (a) Group	C-Cl (b) Group
$f_1$	0.75	1		
$n_1$	2	1	1	1
$n_2$	0	0	0	0
$n_3$	0	0	0	0
$C_1$	0.5	0.75	0.5	0.5
$C_2$	0.85252	1	0.81317	0.81317
$c_1$	1	1	1	1
$c_2$	0.85252	0.91771	1	1
$c_3$	0	1	0	0
$c_4$	3	1	2	2
$c_5$	0	1	0	0
$C_{1o}$	0.5	0.75	0.5	0.5
$C_{2o}$	0.85252	1	0.81317	0.81317
$V_e$ (eV)	-101.12679	-37.10024	-31.85648	-31.85648
$V_p$ (eV)	20.69825	13.17125	8.25686	8.25686
$T$ (eV)	34.31559	11.58941	7.21391	7.21391
$V_m$ (eV)	-17.15779	-5.79470	-3.60695	-3.60695
$E(\text{ar})$ (eV)	0	-14.63489	-14.63489	-14.63489
$\Delta E_{H_2MO}(\text{ar})$ (eV)	0	-1.13379	-2.99216	-2.99216
$E_T(\text{ar})$ (eV)	0	-13.50110	-11.64273	-11.64273
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63539	-31.63539
$E_T(\text{atom} - \text{atom}, msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.72457	-0.72457
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.35994	-32.35994
$\omega$ ( $10^{15}$ rad / s)	49.7272	26.4826	8.03459	14.7956
$E_K$ (eV)	32.73133	17.43132	5.28851	9.73870
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.14722	-0.19978
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.08059 [12]	0.08059 [12]
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.10693	-0.15949
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803
$E_T(\text{Group})$ (eV)	-49.54347	-32.28590	-32.46687	-32.51943
$E_{initial}(e_1 \text{ ar})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(e_3 \text{ ar})$ (eV)	0	-13.59844	0	0
$E_D(\text{Group})$ (eV)	5.63881	3.90454	3.19709	3.24965



Table 15.235. The total bond energies of chlorobenzenes calculated using the functional group composition and the energies of Table 15.234 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_b$  values based on composition is given by (15.58).

Formula	Name	$C \equiv C$	$CH$ (t)	$C-C$ (a)	$C-C$ (b)	$E_{mag}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_5Cl$	Chlorobenzene	6	5	1	0	0	56.5263	56.581	0.00051
$C_6H_4Cl_2$	m-dichlorobenzene	6	4	2	0	0	55.84518	55.832	0.00012
$C_6H_3Cl_3$	1,2,3-trichlorobenzene	6	3	3	0	0	55.13775	55.077	-0.00111
$C_6H_2Cl_4$	1,3,5-trichlorobenzene	6	3	0	1	0	55.29542	55.255	-0.00079
$C_6Cl_6$	Hexachlorobenzene	6	0	6	0	3	52.57130	52.477	-0.00179

Table 15.236. The bond angle parameters of chlorobenzenes and experimental values [1].  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

Atoms/Angle	$2C^1$ Bond 1 ( $a_1$ )	$2C^1$ Bond 2 ( $a_1$ )	$2C^1$ Terminal Atom ( $a_1$ )	$E_{r,calc}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{r,calc}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$\zeta_1$ Atom 1	$\zeta_2$ Atom 2	$\zeta_1$	$\zeta_2$	$\zeta_1$	$\zeta_2$	$\zeta_1$	$\zeta_2$	$E_r$ (eV)	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$\theta_3$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C \equiv C$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	1	0.79232		-1.85836				120.19	120 chlorobenzene 121.7 ( $\angle C \equiv C$ )(C) chlorobenzene 120 [50-52] (benzene)
$\angle C \equiv C$ (aromatic)																				120.19	120 [50-52] (benzene)



## PHENOL

Phenol has the formula  $C_6H_6O$  and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an  $OH$  functional group and a  $C-O$  functional group. The aromatic  $C \equiv C^{3e}$  and  $C-H$  functional groups are equivalent to 5 those of benzene given in Aromatic and Heterocyclic Compounds section. The  $OH$  functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a  $C-O$  functional group that is are solved using the same principles as those used to solve the alcohol functional groups wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  10 shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and  $O$  AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic  $C2sp^3$  HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of 15 the  $C-O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(\text{aryl}C2sp^3HO \text{ to } O) &= \frac{E(O)}{E(C, 2sp^3)} c_2(\text{aryl}C2sp^3HO) \\ &= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \\ &= 0.79329 \end{aligned} \quad (15.150)$$

$E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C-O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-1.49608 \text{ eV}$ . It is based on the energy 20 match between the  $OH$  group and the  $C2sp^3$  HO of an aryl group and is given by the linear combination of  $-0.92918 \text{ eV}$  (Eq. (14.513)) and  $-1.13379 \text{ eV}$  (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of phenol are given in Tables 25 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each  $E_p(\text{group})$  of Table 15.240



corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.79-15.108) are given in Table 15.242.

Table 15.237. The symbols of functional groups of phenol.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C}=C$
CH (aromatic)	CH (i)
Aryl C-O	C-O (a)
OH group	OH

5

Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

Parameter	$\overset{3e}{C}=C$ Group	CH (i) Group	C-O (a) Group	OH Group
$a (a_0)$	1.47348	1.60061	1.68220	1.26430
$c' (a_0)$	1.31468	1.03299	1.29700	0.91808
Bond Length $2c' (\text{\AA})$	1.39140	1.09327	1.37268	0.971651
Exp. Bond Length ( $\text{\AA}$ )	1.397 avg. (phenol)	1.084 (phenol)	1.364 (phenol)	0.956 (phenol)
$b, c (a_0)$	0.66540	1.22265	1.07126	0.86925
$e$	0.89223	0.64537	0.77101	0.72615



Table 15.239. The MO to HO intercept geometrical bond parameters of phenol.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{mp}, A(0))$ .

Bond	Atom	$E_1$ (eV)	$E_2$ (eV)	$E_3$ (eV)	$E_4$ (eV)	Final Total Energy ( $C_{2sp}^3$ ) (eV)	$r_{\text{bond}}$ ( $a_0$ )	$r_{\text{bond}}$ ( $a_0$ )	$E_{\text{atom}}(C_{2sp}^3)$ (eV) Final	$E(C_{2sp}^3)$ (eV) Final	$\theta$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H$ ( $C_1H$ )	$C_1$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.2678	0.21379
$C_1=$ $C_2O-H$	$O$	-0.74804	0	0	0		1.00000	0.87363	-15.57379		115.79	64.21	64.82	0.53799	0.38009
$C_1=$ $C_2O-H$	$C_2$	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$C_1=$ $C_2O-H$	$O$	-0.74804	0	0	0		1.00000	0.87363	15.57379		106.51	73.49	51.43	1.04871	0.24829
$C_1=$ $C_2O-H$	$C_1$	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	133.88	46.12	58.55	0.76870	0.34598
$C_1=$ $C_2O-H$	$C_1$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.73955	0.55553



Table 15.240. The energy parameters (eV) of functional groups of phenol.

Parameters	$\overset{3e}{C=C}$ Group	CH (i) Group	C-O (a) Group	OH Group
$f_1$	0.75	1		
$n_1$	2	1	1	1
$n_2$	0	0	0	0
$n_3$	0	0	0	0
$C_1$	0.5	0.75	0.5	0.75
$C_2$	0.85252	1	1	1
$c_1$	1	1	1	0.75
$c_2$	0.85252	0.91771	0.79329	1
$c_3$	0	1	0	1
$c_4$	3	1	2	1
$c_5$	0	1	0	1
$C_{1o}$	0.5	0.75	0.5	0.75
$C_{2o}$	0.85252	1	1	1
$V_e$ (eV)	-101.12679	-37.10024	-34.04658	-40.92709
$V_p$ (eV)	20.69825	13.17125	10.49024	14.81988
$T$ (eV)	34.31559	11.58941	10.11966	16.18567
$V_m$ (eV)	-17.15779	-5.79470	-5.05983	-8.09284
$E(\lambda O1HO)$ (eV)	0	-14.63489	-14.63489	-13.6181
$\Delta E_{H_2MO}(\lambda O1HO)$ (eV)	0	-1.13379	-1.49608	0
$E_T(\lambda O1HO)$ (eV)	0	-13.50110	-13.13881	-13.6181
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-31.63532	-31.63247
$E_T(atom - atom, msp^3 AO)$ (eV)	-2.26759	-0.56690	-1.49608	0
$E_T(MO)$ (eV)	-65.53833	-32.20226	-33.13145	-31.63537
$\omega$ ( $10^{15}$ rad/s)	49.7272	26.4826	13.3984	44.1776
$E_K$ (eV)	32.73133	17.43132	8.81907	29.07844
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.19465	-0.33749
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12808 [19]	0.46311 [17-18]
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.13061	-0.10594
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.11441
$E_T(Group)$ (eV)	-49.54347	-32.28590	-33.26206	-31.74130
$E_{initial}(e_1 \lambda O1HO)$ (eV)	-14.63489	-14.63489	-14.63489	-13.6181
$E_{initial}(e_2 \lambda O1HO)$ (eV)	0	-13.59844	0	-13.59844
$E_D(Group)$ (eV)	5.63881	3.90454	3.99228	4.41035



Table 15.241. The total bond energies of phenol calculated using the functional group composition and the energies of Table 15.240 compared to the experimental values [2].

Formula	Name	$C^x$	$(^1H)$	$(^1H)$	$(^1H)$	Calculated	Experimental	Relative
$C_6H_6O$	Phenol	6	5	1	1	Total Bond Energy (kJ)	Total Bond Energy (kJ)	Error
						61.5817	61.704	-0.00087

Table 15.242. The bond angle parameters of phenol and experimental values [1].  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{amp}^\circ, \text{kJ})$ .

Atoms of Angle	$2\sigma^1$ Bond 1 ( $a_1$ )	$2\sigma^1$ Bond 2 ( $a_2$ )	$2\sigma^1$ Terminal Atoms ( $a_3$ )	$E_T$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_T$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_1$ Atom 1	$c_2$ Atom 2	$c_1$	$c_2$	$c_1'$	$c_2'$	$E_T$ (eV)	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Calc. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C_1 C_2 C_3$ (aromatic)	2.62956	2.62956	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	1	-1.85356			120.19	120 [50-52] (benzene)
$\angle C_1 C_2 H$ (aromatic)															120.19		119.91	120 [50-52] (benzene)
$\angle C_1 O H$	2.59999	1.85016	3.6815	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0			109.84	109.2 (phenol)



## ANILINE

Aniline and methyl aniline have the formula  $C_6H_7N$  and  $C_7H_9N$ , respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an  $NH_2$  functional group and a  $C-N$  functional group. The aromatic  $C=C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $C-C$  and  $CH_3$  functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino ( $NH_2$ ) functional group was solved using the procedure given in the Dihydrogen Nitride ( $NH_2$ ) section. Using the results of Eqs. (13.245-13.368), the aryl amino parameters in Eq. (15.51) are  $n_1 = 2$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  $C_{1o} = 1.5$ , and  $c_1 = 0.75$ . In the determination of the hybridization factor  $c_2$  of Eq. (15.52) for the  $N-H$ -bond MO of aryl amines, the  $C2sp^3$  HO of the  $C-NH_2$ -bond MO has an energy of  $E(C, 2sp^3) = -15.76868 \text{ eV}$  (Eq. (15.18) corresponding to  $s = 2$  in Eqs. (15.18-15.20), and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $N-H$   $H_2$ -type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  given by Eq. (15.68) is

$$c_2(H \text{ to aniline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171 \quad (15.151)$$

The bond between the amino and aromatic ring comprises a  $C-N$  functional group that is the same as that of  $2^\circ$  amines (methylene) except that the energies corresponding to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and  $N$  AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The hybridization is determined in a similar manner to that of the  $C-O$  group of phenol. In anilines, the aromatic  $C2sp^3$  HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $N$  AO has an energy



of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.51) for the  $C-O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(\text{aryl}C2sp^3HO \text{ to } N) &= \frac{E(N)}{E(C,2sp^3)} c_2(\text{aryl}C2sp^3HO) \\ &= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \\ &= 0.84665 \end{aligned} \quad (15.152)$$

5  $E_r(\text{atom-atom}, msp^3.AO)$  of the  $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.13379 \text{ eV}$  (Eq. (14.247)). It is based on the energy

match between the  $NH_2$  group and the  $C2sp^3$  HO of the aryl group and is twice that of the aryl  $C-H$  group that it replaces.

10 The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in  
15 Table 15.247 was calculated as the sum over the integer multiple of each  $E_p(\text{Group})$  of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.79-15.108) are given in Table 15.248.

20 Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	$CH$ (i)
Aryl C-N	$C-N$ (a)
$NH_2$ group	$NH_2$
$C_a - C_b$ ( $CH_3$ to aromatic bond)	$C-C$ (a)
$CH_3$ group	$C-H$ ( $CH_3$ )



Table 15.244. The geometrical bond parameters of aniline and methyl-substituted anilines and experimental values [1].

Parameter	C=C Group	C-H (i) Group	C-N (a) Group	NH <sub>2</sub> Group	C-C (a) Group	C-H (CH <sub>3</sub> ) Group
$a$ (Å)	1.47348	1.00061	1.81158	1.24428	2.06004	1.04920
$c'$ (Å)	1.31468	1.03299	1.34595	0.94134	1.43528	1.04856
Bond Length $2c'$ (Å)	1.39140	1.09327	1.42449	0.98627	1.51904	1.10974
Exp. Bond Length (phenol) (Å)	1.397 avg. (phenol)	1.084 (phenol)	1.431 (aniline)	0.998 (aniline)	1.524 (toluene)	1.11 (avg.) (toluene)
$b_1 c$ (Å)	0.66540	1.22265	1.21254	0.81370	1.47774	1.27295
$e$	0.89223	0.64537	0.74297	0.75653	0.69673	0.63380

5 Table 15.245. The MO to HO intercept geometrical bond parameters of aniline and methyl-substituted anilines.  $E_r$  is  $E_r$  (atom-atom, msp, AC).

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy (eV)	$r_{\text{final}}$ (Å)	$r_{\text{final}}$ (Å)	$E_{\text{total}}(C2sp^2)$ (eV) Final	$E(C2sp^2)$ (eV) Final	$\theta'$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (Å)	$d_2$ (Å)
C-H (C <sub>1</sub> H)	C <sub>1</sub>	-0.85035	-0.85035	-0.56690	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
C-H (C <sub>1</sub> H <sub>3</sub> )	C <sub>1</sub>	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	79.89	101.11	43.13	1.20567	0.13511
C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> NH-H	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47034	0.46500
C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> -NH <sub>2</sub>	C <sub>1</sub>	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	88.49	91.51	41.01	1.36696	0.02101
C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> -NH <sub>2</sub>	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> -C <sub>3</sub> H <sub>3</sub>	C <sub>1</sub>	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	73.38	106.62	34.97	1.08807	0.23279
C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> -C <sub>3</sub> H <sub>3</sub>	C <sub>1</sub>	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90247	61.56	118.44	28.27	1.81430	0.37901
C <sub>1</sub> =HC <sub>2</sub> C <sub>3</sub>	C <sub>1</sub>	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75855	0.25553



Table 15.246. The energy parameters (eV) of functional groups of aniline and methyl-substituted anilines.

Parameters	$\overset{\text{3e}}{\text{C}}=\text{C}$ Group	CH (i) Group	C - N (a) Group	NH <sub>2</sub> Group	C - C (a) Group	CH <sub>3</sub> Group
$f_1$	0.75	1				
$n_1$	2	1	1	2	1	3
$n_2$	0	0	0	0	0	2
$n_3$	0	0	0	1	0	0
$C_1$	0.5	0.75	0.5	0.75	0.5	0.75
$C_2$	0.85252	1	1	0.93613	1	1
$c_1$	1	1	1	0.75	1	1
$c_2$	0.85252	0.91771	0.84665	0.92171	0.91771	0.91771
$c_3$	0	1	0	0	0	0
$c_4$	3	1	2	1	2	1
$c_5$	0	1	0	2	0	3
$C_{1a}$	0.5	0.75	0.5	1.5	0.5	0.75
$C_{2a}$	0.85252	1	1	1	1	1
$V_e$ (eV)	-101.12679	-37.10024	-32.76465	-78.97795	-29.95792	-107.32728
$V_p$ (eV)	20.69825	13.17125	10.10870	28.90735	9.47952	38.92728
$T$ (eV)	34.31559	11.58941	9.04312	31.73641	7.27120	32.53914
$V_m$ (eV)	-17.15779	-5.79470	-4.52156	-15.86820	-3.63560	-16.26957
$E_{\text{AOIHO}}$ (eV)	0	-14.63489	-14.63489	-14.53414	-15.35946	-15.56407
$\Delta E_{\text{H}_2\text{MO}}$ (AOIHO) (eV)	0	-1.13379	-1.13379	0	-0.56690	0
$E_T$ (AOIHO) (eV)	0	-13.50110	-13.50110	-14.53414	-14.79257	-15.56407
$E(n, \text{AOIHO})$ (eV)	0	0	0	-14.53414	0	0
$E_T(\text{H}_2\text{MO})$ (eV)	-63.27075	-31.63539	-31.63549	-48.73654	-31.63537	-67.69451
$E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{AO})$ (eV)	-2.26759	-0.56690	-1.13379	0	-1.13379	0
$E_T(\text{MO})$ (eV)	-65.53833	-32.20226	-32.76916	-48.73660	-32.76916	-67.69450
$\omega$ ( $10^{15}$ rad / s)	49.7272	26.4826	11.9890	68.9812	16.2731	24.9286
$E_K$ (eV)	32.73133	17.43132	7.89138	45.40465	10.71127	16.40846
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.18211	-0.42172	-0.21217	-0.25352
$\bar{E}_{\text{Kvib}}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.40929 [22]	0.14940 [53]	0.35532 (Eq. (13.458))
$\bar{E}_{\text{osc}}$ (eV)	-0.25982	-0.08364	-0.10462	-0.21708	-0.13747	-0.22757
$E_{\text{mag}}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(\text{Group})$ (eV)	-49.54347	-32.28590	-32.87379	-49.17075	-32.90663	-67.92207
$E_{\text{initial}}(e_1 \text{AOIHO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
$E_{\text{initial}}(e_3 \text{AOIHO})$ (eV)	0	-13.59844	0	-13.59844	0	-13.59844
$E_D(\text{Group})$ (eV)	5.63881	3.90454	3.60401	7.43973	3.63685	12.49186



Table 15.247. The total bond energies of aniline and methyl-substituted anilines calculated using the functional group composition and the energies of Table 15.246 compared to the experimental values [2].

Formula	Name	$\sum C=C$	$\sum C-H$ (i)	$C-N$ (a) Group	$NH_2$ Group	$C-C$ (a) Group	$CH_3$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_5N$	Aniline	6	5	1	1	0	0	64.4373	64.374	-0.00093
$C_7H_7N$	2-methylaniline	6	4	1	1	1	1	76.62345	76.643	-0.00025
$C_8H_9N$	3-methylaniline	6	4	1	1	1	1	76.62345	76.661	0.00050
$C_9H_{11}N$	4-methylaniline	6	4	1	1	1	1	76.62345	76.654	0.00040

Table 15.248. The bond angle parameters of aniline and methyl-substituted anilines and experimental values [1].  $E_T$  is  $E_T(atom - atom, nsp^2, AO)$ .

Atoms of Angle	$2c'$ Bond 1 ( $a_n$ )	$2c'$ Bond 2 ( $a_n$ )	$2c'$ Terminal Atoms ( $a_n$ )	$E_{T(amide)}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{T(amide)}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c'_2$	$E_T$ (eV)	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C' C''$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85536			120.19	120 [50-52] (benzene)
$\angle C' C' H$ (aromatic)																120.19	120 [50-52] (benzene)	
$\angle HNH$	1.86268	1.86268	3.1559	-14.53414	N	H	H	0.95613 $E_{\sigma}(13.248)$	0.84665 $E_{\sigma}(15.152)$	1	1	0.75	1.06823	0		113.89	113.9 (aniline)	
$\angle HNC''$	1.86268	2.69190	4.0332	-14.53414	N		9	0.86284 $E_{\sigma}(15.64)$		0.75	1	0.75	1.01912	0			122.70	



## ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an  $NO_2$  functional group and a  $C-N$  functional group. Examples include nitrobenzene, nitrophenol, and nitroaniline with formulas  $C_6H_5NO_2$ ,  $C_6H_5NO_3$ , and  $C_6H_6N_2O_2$ , respectively. The aromatic  $C \equiv C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $OH$  and  $C-O$  functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The  $NH_2$  and  $C-N$  functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond energies of the nitroanilines given in Table 15.252 are due to differences in the  $E_{osc}$  term. For simplicity and since the differences are small, the  $E_{osc}$  terms for nitroanilines were taken as the same.

The  $NO_2$  group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a  $C-N$  functional group that is the same as that of nitroalkanes given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  is  $-0.72457 eV$ , one half of that of the  $C-N$ -bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  ( $eV$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.79-15.108) are given in Table 15.254.



Table 15.249. The symbols of functional groups of aryl nitro compounds.

Functional Group	Group Symbol
CC (aromatic bond)	${}^{3c}C=C$
CH (aromatic)	CH (i)
Aryl C-N (aniline)	C-N (a)
Aryl C-N (nitro)	C-N (b)
Aryl C-O	C-O (a)
NO <sub>2</sub> group	NO <sub>2</sub>
NH <sub>2</sub> group	NH <sub>2</sub>
OH group	OH

Table 15.250. The geometrical bond parameters of aryl nitro compounds and experimental values [1].

Parameter	${}^{3c}C=C$ Group	CH (i) Group	C-N (a) Group	C-N (b) Group	C-O (a) Group	NO <sub>2</sub> Group	NH <sub>2</sub> Group	OH Group
$a$ ( $a_0$ )	1.47348	1.60061	1.81158	1.97794	1.68220	1.33221	1.24428	1.26430
$c'$ ( $a_0$ )	1.31468	1.03299	1.34595	1.40639	1.29700	1.15421	0.94134	0.91808
Bond Length $2c'$ ( $\text{\AA}$ )	1.39140	1.09327	1.42449	1.48846	1.37268	1.22157	0.99627	0.971651
Exp. Bond Length ( $\text{\AA}$ )	1.397 avg. (phenol)	1.084 (phenol)	1.431 (aniline)		1.364 (phenol)	1.224 (nitromethane)	0.998 (aniline)	0.956 (phenol)
$b, c$ ( $a_0$ )	0.66540	1.22265	1.21254	1.39079	1.07126	0.66526	0.81370	0.86925
$e$	0.89223	0.64537	0.74297	0.71104	0.77101	0.86639	0.75653	0.72615



Table 15.251. The MO to HO intercept geometrical bond parameters of aryl nitro compounds.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{\text{final}}$ (a <sub>0</sub> )	$r_{\text{initial}}$ (a <sub>0</sub> )	$E(C2sp^3)$ (eV) Final	$\theta$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
$C-H(C^H)$	$C^H$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79397	-16.90248	74.42	105.58	38.84	1.24678	0.13179
$(C^H)_2 C^O-H$	$O$	-0.74804	0	0	0		1.00000	0.87363	-15.57379	115.79	64.21	64.82	0.53799	0.38009
$(C^H)_2 C^O-OH$	$C^O$	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$(C^H)_2 C^O-OH$	$O$	-0.74804	0	0	0		1.00000	0.87363	-15.57379	106.51	73.49	51.43	1.04871	0.24829
$(C^H)_2 C^O-OH$	$C^O$	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.08362	133.88	46.12	58.55	0.76870	0.54598
$C^H=HC^O=C^H$	$C^H$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79397	-16.90248	134.24	45.76	58.98	0.75953	0.55553
$C^H=(H^H)_2 C^O=C^H$	$C^O$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79397	-16.90248					
$(C^H)_2 C^O-OH$	$C^O$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79397	-16.90248					
$C^H=(H^H)_2 C^O=C^H$	$C^H$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79397	-16.90248					
$(C^H)_2 C^O-NH-H$	$N$	-0.56690	0	0	0		0.93084	0.88392	-15.39265	121.74	58.26	67.49	0.47654	0.46500
$(C^H)_2 C^O-NH_2$	$C^O$	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79397	-16.90248	88.49	91.51	41.01	1.36096	0.02101
$(C^H)_2 C^O-NH_2$	$N$	-0.56690	0	0	0		0.93084	0.88392	-15.39265	96.32	83.68	46.43	1.24859	0.09756
$(C^H)_2 C^O-H_3$	$C^O$	-0.56690	0	0	0		0.91771	0.88392	-15.39265	73.38	106.62	34.97	1.68807	0.25279
$(C^H)_2 C^O-H_3$	$C^H$	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79397	-16.90247	61.56	118.44	28.27	1.81430	0.37901
$RN(O)=O$	$O$	-0.92918	0	0	0		1.00000	0.86359	-15.75495	135.25	44.75	66.05	0.54089	0.61535
$RN(O)=O$	$N$	-0.92918	-0.92918	-0.36229	0		0.93084	0.79816	-17.04640	132.36	47.64	62.44	0.61640	0.53781
$(C^H)_2 C^O-NO_2$	$C^O$	-0.36229	-0.85035	-0.85035	0	-155.67867	0.91771	0.80561	-16.88873	72.49	107.51	53.55	1.64875	0.24256
$(C^H)_2 C^O-NO_2$	$N$	-0.92918	-0.92918	-0.36229	0		0.93084	0.79816	-17.04640	71.53	108.47	52.98	1.65923	0.25284
$C^H=(O_2N)_2 C^O=C^H$	$C^O$	-0.36229	-0.85035	-0.85035	0	-155.67867	0.91771	0.80561	-16.88873	134.63	45.35	59.47	0.74854	0.56614



Table 15.252. The energy parameters (eV) of functional groups of aryl nitro compounds.

Parameters	$\overset{3*}{C=C}$ Group	CH (I) Group	C-N (a) Group	C-N (b) Group	C-O (a) Group	NO <sub>2</sub> Group	NH <sub>2</sub> Group	OH Group
$f_1$	0.75	1						
$n_1$	2	1	1	1	1	2	2	1
$n_2$	0	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	1	0
$C_1$	0.5	0.75	0.5	0.5	0.5	0.5	0.75	0.75
$C_2$	0.85252	1	1	1	1	1	0.93613	1
$c_1$	1	1	1	1	1	1	0.75	0.75
$c_2$	0.85252	0.91771	0.84665	0.91140	0.79329	0.85987	0.92171	1
$c_3$	0	1	0	0	0	0	0	1
$c_4$	3	1	2	2	2	4	1	1
$c_5$	0	1	0	0	0	0	2	1
$C_{10}$	0.5	0.75	0.5	0.5	0.5	0.5	1.5	0.75
$C_{20}$	0.85252	1	1	1	1	1	1	1
$V_e$ (eV)	-101.12679	-37.10024	-32.76465	-31.36351	-34.04658	-106.90919	-78.97795	-40.92709
$V_p$ (eV)	20.69825	13.17125	10.10870	9.67426	10.49024	23.57588	28.90735	14.81988
$T$ (eV)	34.31559	11.58941	9.04312	7.92833	10.11966	40.12475	31.73641	16.18567
$V_m$ (eV)	-17.15779	-5.79470	-4.52156	-3.96416	-5.05983	-20.06238	-15.86820	-8.09284
$E(\lambda_{OH})$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	0	-14.53414	-13.6181
$\Delta E_{H_2\lambda_{OH}}(\lambda_{OH})$ (eV)	0	-1.13379	-1.13379	-0.72457	-1.49608	0	0	0
$E_T(\lambda_{OH})$ (eV)	0	-13.50110	-13.50110	-13.91032	-13.13881	0	-14.53414	-13.6181
$E(n, \lambda_{OH})$ (eV)	0	0	0	0	0	0	-14.53414	0
$E_T(H_2\lambda_{OH})$ (eV)	-63.27075	-31.63539	-31.63549	-31.63540	-31.63532	-63.27093	-48.73654	-31.63247
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	-0.72457	-1.49608	-3.71673	0	0
$E_T(\lambda_{OH})$ (eV)	-65.53833	-32.20226	-32.76916	-32.35994	-33.13145	-66.98746	-48.73660	-31.63537
$\omega$ ( $10^{15}$ rad / s)	49.7272	26.4826	11.9890	17.8228	13.3984	19.0113	68.9812	44.1776
$E_K$ (eV)	32.73133	17.43132	7.89138	11.73128	8.81907	12.51354	45.40465	29.07844
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.18211	-0.21927	-0.19465	-0.23440	-0.42172	-0.33749
$\bar{E}_{K_{orb}}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.10539 [45]	0.12808 [19]	0.19342 [45]	0.40929 [22]	0.46311 [17-18]
$\bar{E}_{inc}$ (eV)	-0.25982	-0.08364	-0.10462	-0.16658	-0.13061	-0.13769	-0.21708	-0.10594
$E_{mng}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441
$E_T(Grp)$ (eV)	-49.54347	-32.28590	-32.87379	-32.52652	-33.26206	-67.26284	-49.17075	-31.74130
$E_{initial}(c, \lambda_{OH})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-13.6181
$E_{initial}(c, \lambda_{OH})$ (eV)	0	-13.59844	0	0	0	0	-13.59844	-13.59844
$E_D(Grp)$ (eV)	5.63881	3.90454	3.60401	3.25674	3.99228	8.72329	7.43973	4.41035



Table 15.253. The total bond energies of aryl nitro compounds calculated using the functional group composition and the energies of Table 15.252 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighed sum of the  $E_D$  (group) (e) values based on composition is given by (15.58).

Formula	Name	$\sum C=C$	$CH$ (i)	$C-N$ (a)	$C-N$ (b)	$C-O$ (a)	$NO_2$	$NH_2$	$OH$	$E_{mag}$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_5NO_2$	Nitrobenzene	6	5	0	1	0	1	0	0	1	65.18754	65.217	0.00046
$C_6H_4(NO_2)_2$	2,4-dinitrophenol	6	4	0	2	1	2	1	1	2	71.61308	71.642	0.00037
$C_6H_5NO_2$	2-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.424	-0.00050
$C_6H_4(NO_2)_2$	3-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.481	-0.00009
$C_6H_3(NO_2)_3$	4-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.476	-0.00002

Table 15.254. The bond angle parameters of aryl nitro compounds and experimental values [1].  $E_T$  is  $E_T(atom - atom, mp^3 AO)$ .

Atom of Angle	$2c'$ Bond 1 ( $a_1$ )	$2c'$ Bond 2 ( $a_2$ )	$2c'$ Terminal Atom ( $a_3$ )	$E_{terminal}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{terminal}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$\varphi_1$	$\varphi_2$	$E_T$ (eV)	$\theta_1$ (°)	$\theta_2$ (°)	Cal. $\theta$ (°)	Exp. $\theta$ (°)
$\angle CCC$ (aromatic)	2.6936	2.6936	4.585	-17.17218	34	-17.17218	34	0.79332	0.79332	1	1	1	0.79332	-1.85836			120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)															120.19		119.91	120 [50-52] (benzene)
$\angle ONO$	2.30843	2.30843	4.1231	-16.68411	24	-16.68411	24	0.81549	0.81549	1	1	1	0.81549	-1.44915			126.52	123.2 [54] (nitrobenzene)
$\angle CNO$	2.81279	2.30843	4.4159	-17.45562	40	-13.61806	0	0.77945	0.85595 ( $E_T$ (15.114))	1	1	1	0.81670	-1.65376			118.82	125.3 [54] (nitrobenzene)
$\angle C'OH$	2.59399	1.83616	3.6515	-14.82575	1	-14.82575	1	0.91771	0.91771	0.75	1	0.75	0.91771	0			109.84	118.5 [54] (nitrobenzene)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.84665 ( $E_T$ (13.248))	0.84665 ( $E_T$ (13.248))	1	1	1	1.06823	0			113.89	109.0 (phenol)
$\angle C'NH$	2.69190	1.88268	3.9833	-15.95955	9	-14.53414	N	0.84665 ( $E_T$ (15.152))	0.84665 ( $E_T$ (15.152))	0.75	1	0.75	1.00000	0			120.05	113.9 (aniline)



## BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an  $C-C(O)-OH$  moiety that comprises  $C=O$  and  $OH$  functional groups that are the same as those of carboxylic acids given in the corresponding 5 section. The single bond of aryl carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. This group is also equivalent to the same group of carboxylic acids except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-1.29147\text{ eV}$  which is a linear combination of  $\frac{-1.13379\text{ eV}}{2}$ ,  $E_T(atom-atom,msp^3.AO)$  of the  $C-H$  group that the  $C-C(O)$  group replaces, and that 10 of an independent  $C2sp^3\text{ HO}$ ,  $-0.72457\text{ eV}$  (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas  $C_7H_6O_2$ ,  $C_7H_5O_2Cl$ , and  $C_7H_7NO_2$ , respectively. The aromatic  $C\equiv C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic 15 Compounds section. The  $NH_2$  and  $C-N$  functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The  $C-Cl$  functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The  $C-Cl$  functional group of 3 or 4-chlorobenzoic acids corresponding to ortho and para substitution is also equivalent to that of 20 chlorobenzene, except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\text{ eV}$  (Eq. (14.513)) since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the  $C2sp^3\text{ HO}$ .

The symbols of the functional groups of benzoic acid compounds are given in Table 25 15.255. The corresponding designations of benzoic acid is shown in Figure 64. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of



each  $E_D(\text{Group})$  of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.79-15.108) are given in Table 15.260.

5 Table 15.255. The symbols of functional groups of benzoic acid compounds.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C} = C$
CH (aromatic)	CH (i)
C-C(O)	C - C(O)
C=O (aryl carboxylic acid)	C = O
(O)C-O	C - O
OH group	OH
Cl - C (Cl to aromatic bond of 2-chlorobenzoic acid)	C - Cl (i)
Cl - C (Cl to aromatic bond of 3 or 4-chlorobenzoic acid)	C - Cl (ii)
Aryl C-N (aniline)	C - N
NH <sub>2</sub> group	NH <sub>2</sub>



Table 15.256. The geometrical bond parameters of benzoic acid compounds and experimental values [1].

Parameter	C=C Group	CH (i) Group	C-C(O) Group	C=O Group	C-O Group	C-O Group	OH Group	C-Cl (i) Group	C-Cl (ii) Group	C-N Group	NH <sub>2</sub> Group
$a$ ( $a_0$ )	1.47348	1.60061	1.93111	1.29907	1.73490	1.26430	1.26430	2.20799	2.19358	1.81158	1.24428
$c'$ ( $a_0$ )	1.31468	1.03299	1.39682	1.13977	1.31716	0.91808	0.91808	1.64782	1.64243	1.34595	0.94134
Bond Length 2c' ( $\text{\AA}$ )	1.39140	1.09327	1.47833	1.20628	1.39402	0.971651	0.971651	1.74397	1.73827	1.42449	0.99627
Exp. Bond Length ( $\text{\AA}$ )	1.399 (benzene)	1.101 (benzene)	1.48 [55] (benzoic acid)	1.214 (acetic acid)	1.393 (methyl formate)	0.972 (formic acid)	0.972 (formic acid)	1.737 (chlorobenzene)	1.737 (chlorobenzene)	1.431 (aniline)	0.998 (aniline)
$h_c$ ( $a_0$ )	0.66540	1.22265	1.36225	0.62331	1.12915	0.86925	0.86925	1.46967	1.45403	1.21254	0.81370
$e$	0.89223	0.64537	0.71591	0.87737	0.75921	0.72615	0.72615	0.74630	0.74874	0.74297	0.75653



Table 15.257. The MO to HO intercept geometrical bond parameters of benzoic acid compounds.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^2 \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy ( $2sp^2$ ) (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ ) Final	$E_{\text{total}}(\text{Casp})$ (eV) Final	$E(2sp^2)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C^* - H$ ( $C^*H$ )	$C^*$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C^* = HC^* = C^*$	$C^*$														
$C^* = (HCOX^*)C^* = C^*(H)_2$	$C^*$				0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.79595	0.55533
$C^* = (C^*)C^* = C^*(H)$	$C^*$														
$C^* = (H_2N)C^* = C^*(H)$	$C^*$														
$(C^*) = C^*(O)O - H$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75403		115.09	64.91	64.12	0.55182	0.36625
$(C^*) = C^*(O) - OH$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75403		101.32	78.68	48.58	1.14765	0.16930
$(C^*) = C^*(O) - OH$	$C^*$	-0.92918	-1.34946	-0.64574	0	-154.54007	0.91771	0.76652	-17.75013	-17.55927	93.11	86.89	42.68	1.27551	0.04165
$(C^*) = C^*(OH) = O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$(C^*) = C^*(OH) = O$	$C^*$	-1.34946	-0.64574	-0.92918	0	-154.54007	0.91771	0.76652	-17.75013	-17.55927	134.03	45.97	62.14	0.60699	0.53278
$C^* = (HCOX^*)C^* = C^*$ ( $C^*$ bound to H, Cl, or $NH_2$ )	$C^*$	-0.64574	-0.83035	-0.83035	0	-153.56212	0.91771	0.79232	-17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124
$(C^*) = (C^* - Cl)$	Cl	-0.36229	0	0	0		1.05158	0.89582	15.18804		82.92	97.08	37.22	1.75824	0.11042
$(C^*) = (C^* - Cl)$	$C^*$	-0.36229	-0.83035	-0.83035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	73.32	106.68	31.67	1.87911	0.23129
$C^* = (C^*)C^* = C^*$ ( $C^*$ bound to H or Cl)	$C^*$	-0.36229	-0.83035	-0.83035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45.35	50.47	0.74854	0.56614
$(C^*) = C^*NH - H$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$(C^*) = C^* - NH_2$	$C^*$	-0.56690	-0.83035	-0.83035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	88.49	91.51	41.01	1.36696	0.02101
$(C^*) = C^* - NH_2$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$C^* = (H_2N)C^* = C^*$	$C^*$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533



Table 15.238. The energy parameters (eV) of functional groups of benzoic acid compounds.

Parameters	C=C Group	C-H (i) Group	C-C(O) Group	C=O Group	C-O Group	OH Group	C-Cl (i) Group	C-Cl (ii) Group	C-N Group	NH <sub>2</sub> Group
$I_1$	0.75	1								
$n_1$	2	1	1	2	1	1	1	1	1	2
$n_2$	0	0	0	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0	0	0	1
$c_1$	0.5	0.75	0.5	0.5	0.5	0.75	0.5	0.5	0.5	0.75
$c_2$	0.85252	1	1	1	1	1	0.81317	0.81317	1	0.95613
$c_3$	1	1	1	1	1	0.75	1	1	1	0.75
$c_4$	0.85252	0.91771	0.91771	0.85395	0.85395	1	1	1	0.84665	0.92171
$c_5$	0	1	0	2	0	1	0	0	0	0
$c_6$	3	1	2	4	2	1	2	2	2	1
$c_7$	0	1	0	0	0	1	0	0	0	2
$c_8$	0.5	0.75	0.5	0.5	0.5	0.75	0.5	0.5	0.5	1.5
$c_9$	0.85252	1	1	1	1	1	0.81317	0.81317	1	1
$V_1$ (eV)	-101.12679	-37.10024	-32.15216	-111.25473	-35.08488	-40.92709	-31.85648	-32.14474	-32.76465	-78.97795
$V_2$ (eV)	20.69825	13.17125	9.74055	23.87467	10.32968	14.81988	8.2686	8.28394	10.10870	28.90735
$T$ (eV)	34.31559	11.58941	8.23945	42.82081	10.11150	16.18567	7.21391	7.32700	9.04312	31.73641
$V_3$ (eV)	-17.15779	-5.79470	-4.11973	-21.41040	-5.0575	-8.09284	-3.60695	-3.66350	-4.52156	-15.86820
$E_1$ (eV)	0	-14.63489	-14.63489	0	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.53414
$\Delta E_{1/2}$ (eV)	0	-1.13379	-1.29147	-2.69893	-2.69893	0	-2.99216	-2.99216	-1.13379	0
$E_2$ (eV)	0	-13.50110	-13.34342	2.69893	-11.93596	-13.6181	-11.64273	-11.64273	-13.50110	-14.53414
$E_3$ (eV)	0	0	0	0	0	0	0	0	0	-14.53414
$E_4$ (eV)	-63.27075	-31.63539	-31.63530	-63.27074	-31.63541	-31.63247	-31.63539	-31.63542	-31.63549	-48.73654
$E_5$ (eV)	-2.26759	-0.56690	-1.29147	-2.69893	-1.85836	0	-0.72457	-0.92918	-1.13379	0
$E_6$ (eV)	-65.53833	-32.70226	-32.92684	-65.96966	-33.49373	-31.63537	-32.35994	-32.56455	-32.76916	-48.73660
$\omega$ [ $10^{15}$ rad/s]	49.7272	26.4826	10.7262	59.4034	24.3637	44.1776	8.03459	8.11389	11.9890	68.9812
$E_7$ (eV)	32.73133	17.43132	7.06019	39.10034	16.03660	29.07844	5.28851	5.34070	7.89138	45.40465
$E_8$ (eV)	-0.35806	-0.26130	-0.17309	-0.40804	-0.26535	-0.33749	-0.14722	-0.14888	-0.18211	-0.42172
$E_9$ (eV)	0.19649	0.35532	0.10502	0.21077	0.14010	0.46311	0.08059	0.08059	0.15498	0.40929
$E_{10}$ (eV)	149	13.458	29	12	31	117-181	1121	1121	1541	221
$E_{11}$ (eV)	-0.25982	-0.08364	-0.12058	-0.30266	-0.19530	-0.10594	-0.10693	-0.10839	-0.10462	-0.21708
$E_{12}$ (eV)	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803
$E_{13}$ (eV)	-49.54347	-32.28590	-33.04742	-66.57498	-33.68903	-31.74130	-32.46687	-32.67314	-32.87379	-49.17075
$E_{14}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.53414
$E_{15}$ (eV)	0	-13.59844	0	0	0	-13.59844	0	0	0	-13.59844
$E_{16}$ (eV)	5.63881	3.90454	3.77764	7.80660	4.41925	4.41035	3.19709	3.40356	3.60401	7.43973



Table 15.259. The total bond energies of benzoic acid compounds calculated using the functional group composition and the energies of Table 15.258 compared to the experimental values [2].

Formula	Name	C=C Group	C-H (i) Group	C-C(O) Group	C=O Group	C-O Group	O-H Group	C-Cl (i) Group	C-Cl (ii) Group	C-N Group	NH <sub>2</sub> Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub>	Benzoic acid	6	3	1	1	1	1	0	0	0	0	73.6038	73.762	-0.00009
C <sub>6</sub> H <sub>4</sub> ClCO <sub>2</sub>	2-chlorobenzoic acid	6	4	1	0	1	1	1	0	0	0	73.06193	73.082	0.00027
C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> CO <sub>2</sub>	3-chlorobenzoic acid	6	4	1	0	1	1	0	0	0	0	73.26820	73.261	-0.00010
C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> CO <sub>2</sub>	4-chlorobenzoic acid	6	4	1	1	1	1	0	0	0	0	73.26820	73.247	-0.00028
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	Aniline-2-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.941	0.00041
C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	Aniline-3-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.813	-0.00118
C <sub>6</sub> H <sub>3</sub> NO <sub>2</sub>	Aniline-4-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.949	0.00030

Table 15.260. The bond angle parameters of benzoic acid compounds and experimental values [1]. E<sub>r</sub> is E<sub>r</sub>(atom-atom, mp<sup>3</sup>, A.O.).

Atoms of Angle	2c <sup>a</sup> Bond 1 (a <sub>0</sub> )	2c <sup>a</sup> Bond 2 (a <sub>0</sub> )	2c <sup>a</sup> Terminal Atoms (a <sub>0</sub> )	E <sub>r</sub> (atom-atom, mp <sup>3</sup> , A.O.)	Atom 1 Hybridization Designation (Table 15.3.A)	F <sub>terminal</sub> Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	S <sub>2</sub> Atom 1	S <sub>2</sub> Atom 2	C <sub>1</sub>	C <sub>2</sub>	γ <sub>1</sub>	γ <sub>2</sub>	E <sub>r</sub> (eV)	θ <sub>r</sub> (°)	θ <sub>1</sub> (°)	θ <sub>2</sub> (°)	Cal θ (°)	Exp. θ (°)
ZC(C)(aromatic)	2.62956	2.62956	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.83836				120.19	120 [50-52] (benzene)
ZC(C)(aromatic)																		119.91	120 [50-52] (benzene)
ZC(C)(aromatic)	2.63431	1.82616	3.6405	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				107.71	
ZC(C)(aromatic)	2.82796	2.27954	4.4721	-17.17218	34	-17.17218	34	0.79232	0.83395 (E <sub>0</sub> , (15.114))	1	1	1	0.82313	-1.65376				121.86	122 [55] (benzoic acid)
ZC(C)(aromatic)	2.82796	2.63431	4.6690	-16.40067	19	-16.40067	19	0.82959	0.83395 (E <sub>0</sub> , (15.114))	1	1	1	0.84177	-1.65376				117.43	118 [55] (benzoic acid)
ZC(C)(aromatic)	2.37954	2.63431	4.3818	-16.17521	12	-16.17521	12	0.84115	0.86339	1	1	1	0.85237	-1.44915				126.03	122 [55] (benzoic acid)
ZC(C)(aromatic)																			120
ZC(C)(aromatic)	2.62956	2.62956	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.83836				120.19	(ZCC(H)C chlorobenzene) 121.7 (ZCC(C)C chlorobenzene) 120 [50-52] (benzene)
ZC(C)(aromatic)																		119.91	120 [50-52] (benzene)
ZHNH	1.88268	1.88268	3.1559	-14.53414	N	-14.53414	N	0.95615 (E <sub>0</sub> , (13.240))	0.84665 (E <sub>0</sub> , (15.152))	1	1	0.75	1.06823	0				113.89	113.9 (aniline)
ZC(NH)	2.69190	1.88268	3.9855	-15.95955	9	-15.95955	9	0.95615 (E <sub>0</sub> , (13.240))	0.84665 (E <sub>0</sub> , (15.152))	0.75	1	0.75	1.06800	0				120.05	



## ANISOLE

Anisole has the formula  $C_7H_8O$  and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety  $-O-CH_3$  to form an ether comprising aromatic and methyl functional groups as well as two types of  $C-O$  functional groups, one for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic  $C \equiv C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $CH_3$  and methyl  $C-O$  functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The  $C-O$  functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether  $C-O$  functional group except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-1.13379 \text{ eV}$  (Eq. (14.247)).  $E_T(atom-atom,msp^3.AO)$  is based on the energy match between the  $OCH_3$  group and the  $C2sp^3$  HO of the aryl group and is twice that of the aryl  $C-H$  group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each  $E_D(Grp)$  of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.79-15.108) are given in Table 15.266.

Table 15.261. The symbols of functional groups of anisole.

Functional Group	Group Symbol
CC (aromatic bond)	$C \equiv C$
CH (aromatic)	$CH$ (i)
Aryl C-O	$C-O$ (a)
Methyl C-O	$C-O$ (b)
$CH_3$ group	$C-H$ ( $CH_3$ )



Table 15.262. The geometrical bond parameters of anisole and experimental values [1].

Parameter	C=C Group	C-H (i) Group	C-O (a) Group	C-O (b) Group	C-H (CH <sub>3</sub> ) Group
$a$ (Å)	1.47348	1.60061	1.82682	1.80717	1.64920
$c'$ (Å)	1.31468	1.03299	1.35160	1.34431	1.04836
Bond Length $2c'$ (Å)	1.39140	1.09327	1.43047	1.42276	1.10974
Exp. Bond Length (phenol) (Å)	1.397 avg.	1.084			1.11 (avg.)
	(phenol)				(toluene)
$b_1 c'$ (Å)	0.66540	1.22265	1.22900	1.20776	1.27295
$e$	0.89223	0.64537	0.75986	0.74388	0.63580

Table 15.263. The MO to HO intercept geometrical bond parameters of anisole.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, AO)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C2sp^2$ (eV)	$r_{\text{final}}$ (Å)	$E_{\text{total}}(C2sp^2)$ (eV) Final	$E(C2sp^2)$ (eV) Final	$\theta'$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (Å)	$d_2$ (Å)
C'-H (C <sub>1</sub> H)	C'	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	74.42	105.38	38.84	1.24678	0.21379
C'-H (OC <sub>1</sub> H <sub>3</sub> )	C'	-0.72457	0	0	0	-152.34026	0.91771	-15.53033	-15.35946	78.85	101.15	42.40	1.21777	0.16921
(C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> O-C <sub>6</sub> H <sub>5</sub>	C'	-0.72457	0	0	0	-152.34026	0.91771	-15.53033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
(C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> O-C <sub>6</sub> H <sub>5</sub>	O	-0.72457	-0.56690	0	0		1.00000	-16.11722		93.38	86.62	44.25	1.29456	0.04975
(C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> -OC <sub>6</sub> H <sub>5</sub>	C'	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	-17.09334	-16.90248	87.00	93.00	40.30	1.39529	0.04170
(C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> -OC <sub>6</sub> H <sub>5</sub>	O	-0.56690	-0.72457	0	0		1.00000	-16.11722		91.59	88.41	43.36	1.32814	0.02346
(C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> OC <sub>6</sub> H <sub>5</sub>	C'	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
(C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> OC <sub>6</sub> H <sub>5</sub>	C'	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533



Table 15.264. The energy parameters (eV) of functional groups of anisole.

Parameters	C=C Group	CH (i) Group	C-O (a) Group	C-O (b) Group	CH <sub>3</sub> Group
$f_i$	0.75	1			
$n_1$	2	1	1	1	3
$n_2$	0	0	0	0	2
$n_3$	0	0	0	0	0
$C_1$	0.5	0.75	0.5	0.5	0.75
$C_2$	0.85252	1	1	1	1
$c_1$	1	1	1	1	1
$c_2$	0.85252	0.91771	0.85395	0.85395	0.91771
$c_3$	0	1	0	0	0
$c_4$	3	1	2	2	1
$c_5$	0	1	0	0	3
$C_{10}$	0.5	0.75	0.5	0.5	0.75
$C_{10}$	0.85252	1	1	1	1
$V_r$ (eV)	-101.12679	-37.10024	-32.67197	-33.15757	-107.32728
$V_r$ (eV)	20.69825	13.17125	10.06645	10.12103	38.92728
$T$ (eV)	34.31559	11.58941	8.94231	9.17389	32.53914
$V_m$ (eV)	-17.15779	-5.79470	-4.47115	-4.58695	-16.26957
$E_{\text{atom}}$ (eV)	0	-14.63489	-14.63489	-14.63489	-15.56407
$\Delta E_{H_{2,sp}}$ (eV)	0	-1.13379	-1.13379	-1.44915	0
$E_r(\text{atom})$ (eV)	0	-13.50110	-13.50110	-13.18574	-15.56407
$E_r(\mu_{1,sp})$ (eV)	-63.27075	-31.63539	-31.63547	-31.63533	-67.69451
$E_r(\text{atom} - \text{atom}, nsp^3, AO)$ (eV)	-2.26759	-0.56690	-1.13379	-1.44915	0
$E_r(\text{sp})$ (eV)	-65.53833	-32.20226	-32.76916	-33.08452	-67.69450
$\omega$ ( $10^{15}$ rad/s)	49.7272	26.4826	11.8393	12.0329	24.9286
$E_s$ (eV)	32.73133	17.43132	7.79284	7.92028	16.40846
$\bar{E}_b$ (eV)	-0.35806	-0.26130	-0.18097	-0.18420	-0.25352
$\bar{E}_{\text{vib}}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.13663 [21]	0.13663 [21]	0.35532 (Eq. (13.458))
$\bar{E}_{\text{vib}}$ (eV)	-0.25982	-0.08364	-0.11266	-0.11589	-0.22757
$E_{\text{vib}}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803
$E_r(\text{vib})$ (eV)	-49.54347	-32.28590	-32.88182	-33.20040	-67.92207
$E_{\text{vib}}(r, \text{vib})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{vib}}(r, \text{vib})$ (eV)	0	-13.59844	0	0	-13.59844
$E_p(\text{vib})$ (eV)	5.63881	3.90454	3.61204	3.93062	12.49186



Table 15.265. The total bond energies of anisole calculated using the functional group composition and the energies of Table 15.264 compared to the experimental values [2].

Formula	Name	$\text{C}^\bullet\text{--C}$	$\text{C--H}$ (i)	$\text{C--O}$ (a)	$\text{C--O}$ (b)	$\text{CH}_3$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$\text{C}_6\text{H}_5\text{O}$	Anisole	6	5	1	1	1	73.3906	73.355	-0.0047

Table 15.266. The bond angle parameters of anisole and experimental values [1].  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mp}^2, \text{AO})$ .

Atoms of Angle	$2c^1$ Bond 1 ( $a_1$ )	$2c^2$ Bond 2 ( $a_2$ )	$2c^3$ Terminal Atoms ( $a_3$ )	$E_{\text{calculated}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3 A)	$E_{\text{calculated}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3 A)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c_2'$	$E_T$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle\text{CCC}$ (aromatic)	2.62936	2.62936	4.585	-17.17218	34	-17.17218	34 (Table 15.3 A)	0.79232	0.79232	1	1	1	0.79232	-1.83836				120.19	120 [50-52] (benzene)
$\angle\text{CCH}$ (aromatic)																	120.19	119.91	120 [50-52] (benzene)



## PYRROLE

Pyrrole having the formula  $C_4H_5N$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to a  $NH$  functional group. The two symmetrical carbon-to-nitrogen bonds comprise the  $C-N-C$  functional group. The 1,3-butdiene moiety comprises  $C-C$ ,  $C=C$ , and  $CH$  functional groups. The  $C-C$  and  $C=C$  groups are equivalent to the corresponding groups of 1,3-butdiene given in the Cyclic and Conjugated Alkenes section except that the energies terms of the corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-butdiene except that the hybridization terms  $c_2$  of the  $C-C$  and  $C=C$  groups and  $C_2$  and  $C_{2o}$  of the  $C=C$  group in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $(C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = 0.85252)$ , in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond character in the carbon-heteroatom bonding.

The  $NH$  group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term  $c_2$  is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the  $CH$  functional group is equivalent to that of 1,3-butdiene, except that  $\Delta E_{H_2MO}(AO/HO) = -2.26758 \text{ eV}$  (Eq. (14.247)) in Eq. (15.42) in order to provide matching double-bond character.

The solution of the  $C-N-C$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the  $C-N-C$  bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO \text{ to } N) = 0.84665$  (Eq. (15.152)) matches the double-bond character of the  $C2sp^3$  HOs to the  $N$  atom of the  $NH$  group, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52)



become that of benzene given by Eq. (15.143),  $C_2(\text{benzene}C2sp^3HO) = 0.85252$ . Furthermore,  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  in Eq. (15.52) are both  $-0.92918 \text{ eV}$  (Eq. (14.513)) per atom corresponding to  $-3.71673 \text{ eV}$  in total. This is the maximum energy for a single bond and corresponds to methylene character 5 as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 65. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of 10 pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.79-15.108) are given in Table 15.272.

15 Table 15.267. The symbols of functional groups of pyrrole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C = C$
$C_b - C_b$	$C - C$
$C_a - N - C_a$	$C - N - C$
NH group	$NH$
CH	$CH$



Table 15.268. The geometrical bond parameters of pyrrole and experimental values [1].

Parameter	C = C Group	C - C Group	C - N - C Group	NH Group	CH Group
$a$ ( $a_0$ )	1.45103	1.77965	1.43222	1.24428	1.53380
$c'$ ( $a_0$ )	1.30463	1.33404	1.29614	0.94134	1.01120
Bond Length $2c'$ ( $\text{\AA}$ )	1.38076	1.41188	1.37178	0.996270	1.07021
Exp. Bond Length ( $\text{\AA}$ )	1.382 (pyrrole)	1.417 (pyrrole)	1.370 (pyrrole)	0.996 (pyrrole)	1.076 (pyrrole)
$b, c$ ( $a_0$ )	0.63517	1.17792	0.60931	0.81370	1.15326
$e$	0.89910	0.74961	0.90499	0.75653	0.65928



Table 15.269. The MO to HO intercept geometrical bond parameters of pyrrole.  $R_i$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy C2sp <sup>3</sup> (eV)	$r_{bond}$ (a <sub>0</sub> )	$E_{bond}$ (C2sp <sup>3</sup> ) (eV) Final	$E$ (C2sp <sup>3</sup> ) (eV) Final	$\theta^*$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ (a <sub>0</sub> )	$d_2$ (a <sub>0</sub> )
C'-H (C'H)	C'	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	-16.69786	83.33	96.65	43.94	1.10452	0.09331
C'-H (C'H)	C'	-1.13380	-1.13380	0	0	-153.88328	0.91771	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
C'-C(H)C'-C'(H)C'-C'	C'	-1.13380	-1.13380	0	0	-153.88328	0.91771	-17.09334	-16.90248	91.37	88.43	42.49	1.31226	0.02177
C'-C(H)C'(H)C'-C'	C'	-1.13380	-1.13380	0	0	-153.88328	0.91771	-17.09334	-16.90248	136.36	43.64	59.86	0.72837	0.57606
HNC'-C'(H)	C'	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.38678
C'(H)N-C'-C'(H)	C'	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	-16.69786	138.54	41.46	61.09	0.69238	0.60376
C'(H)N-C'-C'(H)	N	-0.92918	-0.92918	0	0		0.93084	-16.68411		138.92	41.08	61.59	0.68147	0.61467
N-H (NH)	N	-0.92918	-0.92918	0	0		0.93084	-16.68411		117.34	62.66	62.90	0.56678	0.37456



Table 15.270. The energy parameters (eV) of functional groups of pyrrole.

Parameters	C = C Group	C - C Group	C - N - C Group	NH Group	CH Group
$n_1$	2	1	2	1	1
$n_2$	0	0	0	0	0
$n_3$	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75	0.75
$C_2$	0.85252	1	0.85252	0.93613	1
$c_1$	1	1	1	0.75	1
$c_2$	0.85252	0.85252	0.84665	0.92171	0.91771
$c_3$	0	0	0	1	1
$c_4$	4	2	4	1	1
$c_5$	0	0	0	1	1
$C_{10}$	0.5	0.5	0.5	0.75	0.75
$C_{20}$	0.85252	1	0.85252	1	1
$V_e$ (eV)	-104.37986	-33.80733	-106.58684	-39.48897	-39.09538
$V_p$ (eV)	20.85777	10.19898	20.99432	14.45367	13.45505
$T$ (eV)	35.96751	9.49831	37.21047	15.86820	12.74462
$V_m$ (eV)	-17.98376	-4.74915	-18.60523	-7.93410	-6.37231
$E(\text{AOIHO})$ (eV)	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_2MO}(\text{AOIHO})$ (eV)	-2.26759	-1.85836	-3.71673	0	-2.26758
$E_r(\text{AOIHO})$ (eV)	2.26759	-12.77653	3.71673	-14.53414	-12.36731
$E_r(H_2MO)$ (eV)	-63.27075	-31.63572	-63.27056	-31.63534	-31.63533
$E_r(\text{atom} - \text{atom}, msp^3 AO)$ (eV)	-2.26759	-2.26759	-3.71673	0	0
$E_r(MO)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537	-31.63537
$\omega$ ( $10^{13}$ rad / s)	15.4421	12.3131	15.7474	48.7771	28.9084
$E_K$ (eV)	10.16428	8.10471	10.36521	32.10594	19.02803
$\bar{E}_D$ (eV)	-0.20668	-0.19095	-0.21333	-0.35462	-0.27301
$\bar{E}_{Kvib}$ (eV)	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.40696 [24]	0.39427 [56]
$\bar{E}_{osc}$ (eV)	-0.11720	-0.11680	-0.15754	-0.15115	-0.07587
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803
$E_r(\text{Group})$ (eV)	-65.77272	-34.01976	-67.30254	-31.78651	-31.71124
$E_{initial}(c_1 \text{ AOIHO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{initial}(c_2 \text{ AOIHO})$ (eV)	0	0	0	-13.59844	-13.59844
$E_p(\text{Group})$ (eV)	7.23317	4.74998	8.76298	3.51208	3.32988



Table 15.271. The total bond energies of pyrrole calculated using the functional group composition and the energies of Table 15.270 compared to the experimental values [2].

Formula	Name	$C-C$	$C-N-C$	$NH$	$CH$
$C_4H_5N$	Pyrrole	2	1	1	4
		Calculated Total Bond Energy (eV)		Experimental Total Bond Energy (eV)	
		44.81090		44.785	
				Relative Error	
				-0.00057	

Table 15.272. The bond angle parameters of pyrrole and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(atom - atom, exp, AC)$ .

Atoms of Angle	$2c^1$ Bond 1 ( $\sigma_b$ )	$2c^2$ Bond 2 ( $\sigma_b$ )	$2c^3$ Terminal Atoms ( $\sigma_a$ )	$E_r$ Atom 1 (Table 15.3.B)	Atom 1 Hybridization Designation (Table 15.3.B)	$F_r$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	$c_2$ Atom 1	$c_2$ Atom 2 (Eq. 15.151)	$C_1$	$C_2$	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$\theta_r$ ( $^\circ$ )	$E_T$ (eV)	$c'_2$	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Calc. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle HC-N$	2.02241	2.59228	4.0166	-14.82575	1	-14.53414	N	0.91771	0.92171 (Eq. 15.151)	0.75	1	0.75	1.00435	0	0	1.00435	120.51	107.52	120.51	121.5 (pyrrole)
$\angle C-C-H_a$												120.51	107.52	131.97						
$\angle HNC$	1.88268	2.59228	3.8987	-14.53414	N	-16.49325	6	0.84665 (Eq. 15.152)	0.82493 (Eq. 15.152)	0.75	1	0.75	0.97435	0	0	0.97435	120.37		120.37	
$\angle H_1C-C_1$	2.02241	2.68007	4.2111	-16.88873 $C_s$	15	-15.95954 $C_s$	6	0.80561	0.85252	0.75	1	0.75	1.05822	0	0	1.05822	127.20		127.20	127.1 (pyrrole)
$\angle H_1C-C_1$	2.02241	2.60925	4.2111	-16.88873 $C_u$	15	-15.95954 $C_b$	6	0.80561	0.85252	0.75	1	0.75	1.05822	0	0	1.05822	130.36		130.36	
$\angle H_1C-C_u$	2.02241	2.60925	4.1312	-17.09534 $C_b$	18	-16.47951 $C_u$	11	0.79597	0.82562	0.75	1	0.75	1.03725	0	0	1.03725	125.76		125.76	127.1 (pyrrole)
$\angle C-C-H_a$												125.76	107.01	127.23						
$\angle NC-C_1$	2.59228	2.60925	4.1952	-14.53414	N	-17.09334 $C_b$	18	0.84665 (Eq. 15.152)	0.79597	1	1	1	0.82131	-1.44915		0.82131	107.52	107.7 (pyrrole)	107.52	107.7 (pyrrole)
$\angle C-NC_u$	2.59228	2.59228	4.2426	-17.81791	26	-17.81791	26	0.76560	0.76560	1	1	1	0.76560	-1.83536		0.76560	109.83	109.8 (pyrrole)	109.83	109.8 (pyrrole)
$\angle C-C-C_1$	2.60925	2.68007	4.2426	-17.81791	26	-18.02252	29	0.76560	0.75495	1	1	1	0.75927	-1.83536		0.75927	107.01	107.4 (pyrrole)	107.01	107.4 (pyrrole)



## FURAN

Furan having the formula  $C_4H_4O$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the  $C-O-C$  functional group. The 1,3-butdiene moiety  
5 comprises  $C-C$ ,  $C=C$ , and  $CH$  functional groups. The  $CH$ ,  $C-C$ , and  $C=C$  groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The  $C-O-C$  functional group of furan is solved in a similar manner as that of the  $C-N-C$  group of pyrrole. The solution of the  $C-O-C$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy  
10 minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the  $C-O-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(\text{aryl}C2sp^3HO \text{ to } O) = 0.79329$  (Eq. (15.150)) matches the double-  
15 bond character of the  $C2sp^3$  HOs to the  $O$  atom, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(\text{benzene}C2sp^3HO) = 0.85252$ . Furthermore,  $E_T(\text{atom-atom}, msp^3.AO)$  in Eq. (15.52) is  $-0.92918 \text{ eV}$  (Eq. (14.513)) per atom corresponding to  $-3.71673 \text{ eV}$  in total.

The symbols of the functional groups of furan are given in Table 15.273. The  
20 structure of furan is shown in Figure 66. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.276 corresponding to functional-group composition of the molecule.  
25 The bond angle parameters of furan determined using Eqs. (15.79-15.108) are given in Table 15.278.



Table 15.273. The symbols of functional groups of furan.

Functional Group	Group Symbol
$C_s = C_s$ double bond	$C = C$
$C_s - C_s$	$C - C$
$C_s - O - C_s$	$C - O - C$
$CH$	$CH$

Table 15.274. The geometrical bond parameters of furan and experimental values [1].

Parameter	$C = C$	$C - C$	$C - O - C$	$CH$
$a$ ( $a_0$ )	1.45103	1.77965	1.41546	1.53380
$c'$ ( $a_0$ )	1.30463	1.33404	1.28854	1.01120
Bond Length	1.38076	1.41188	1.36373	1.07021
Exp. Bond Length ( $\text{\AA}$ )	1.361 (furan)	1.431 (furan)	1.362 (furan)	1.075 (furan)
$h, c$ ( $a_0$ )	0.63517	1.17792	0.58583	1.15326
$e$	0.89910	0.74961	0.91033	0.65928

Table 15.275. The MO to HO intercept geometrical bond parameters of furan.  $R_i$  is an alkyl group and  $R, R', R''$  are  $H$  or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{coreval}}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C - H$ ( $C_s H$ )	$C_s$	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C - H$ ( $C_s H$ )	$C_s$	-1.13380	-1.13380	0	0	-153.88328	0.91771	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_s = (H)C_s - C_s(H) = C_s$	$C_s$	-1.13380	-1.13380	0	0	-153.88328	0.91771	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_s = C_s(H)(H)C_s = C_s$	$C_s$	-1.13380	-1.13380	0	0	-153.88328	0.91771	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$OC_s = C_s(H)$	$C_s$	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C_s O - C_s = C_s(H)$	$C_s$	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	-16.69786	140.16	39.84	61.75	0.66992	0.61862
$C_s O - C_s = C_s(H)$	$O$	-0.92918	-0.92918	0	0	-153.67867	1.00000	-16.68411		140.52	39.48	62.25	0.65906	0.62947



Table 15.276. The energy parameters (eV) of functional groups of furan.

Parameters	C = C Group	C - C Group	C - O - C Group	CH Group
$n_1$	2	1	2	1
$n_2$	0	0	0	0
$n_3$	0	0	0	0
$C_1$	0.5	0.5	0.5	0.75
$C_2$	0.85252	1	0.85252	1
$c_1$	1	1	1	1
$c_2$	0.85252	0.85252	0.79329	0.91771
$c_3$	0	0	0	1
$c_4$	4	2	4	1
$c_5$	0	0	0	1
$C_{1a}$	0.5	0.5	0.5	0.75
$C_{2a}$	0.85252	1	0.85252	1
$V_e$ (eV)	-104.37986	-33.80733	-102.49036	-39.09538
$V_p$ (eV)	20.85777	10.19898	21.11822	13.45505
$T$ (eV)	35.96751	9.49831	36.20391	12.74462
$V_m$ (eV)	-17.98376	-4.74915	-18.10196	-6.37231
$E_{(AO/HO)}$ (eV)	0	-14.63489	0	-14.63489
$\Delta E_{H_2MO(AO/HO)}$ (eV)	-2.26759	-1.85836	0	-2.26758
$E_T(AO/HO)$ (eV)	2.26759	-12.77653	0	-12.36731
$E_T(H_2MO)$ (eV)	-63.27075	-31.63572	-63.27019	-31.63533
$E_T(atom - atom, msp^3.AO)$ (eV)	-2.26759	-2.26759	-3.71673	0
$E_T(MO)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537
$\omega$ ( $10^{15}$ rad / s)	15.4421	12.3131	58.0664	28.9084
$E_K$ (eV)	10.16428	8.10471	38.22034	19.02803
$\bar{E}_D$ (eV)	-0.20668	-0.19095	-0.40965	-0.27301
$\bar{E}_{Kvib}$ (eV)	0.17897 [6]	0.14829 [48]	0.12523 [57]	0.39427 [56]
$\bar{E}_{usc}$ (eV)	-0.11720	-0.11680	-0.34704	-0.07587
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803
$E_T(group)$ (eV)	-65.77272	-34.01976	-67.68154	-31.71124
$E_{initial}(c_4 AO/HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5 AO/HO)$ (eV)	0	0	0	-13.59844
$E_D(group)$ (eV)	7.23317	4.74998	9.14198	3.32988



Table 15.277. The total bond energies of furan calculated using the functional group composition and the energies of Table 15.276 compared to the experimental values [2].

Name	C=C		C-C		C-O-C		CH		Relative Error	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
C <sub>4</sub> H <sub>4</sub> O	41.692	41.692	41.6782	41.692	41.692	41.692	41.692	41.692	0.0033	0.0033

Table 15.278. The bond angle parameters of furan and experimental values [1]. In the calculation of  $\theta_v$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(atom-atom, msp, AO)$ .

Atoms of Angle	2a <sup>1</sup> Bond 1 (a <sub>0</sub> )	2a <sup>2</sup> Bond 2 (a <sub>0</sub> )	2c <sup>1</sup> Terminal Atom (a <sub>0</sub> )	E <sub>Calc</sub> Atom 1 (eV)	Atom 1 Hybridization Designation (Table 15.3.B)	E <sub>Calc</sub> Atom 2 (eV)	Atom 2 Hybridization Designation (Table 15.3.B)	c <sub>2</sub> Atom 1	c <sub>2</sub> Atom 2	C <sub>1</sub>	C <sub>2</sub>	c <sub>1</sub>	c <sub>2</sub>	E <sub>r</sub> (eV)	θ <sub>v</sub> (°)	θ <sub>1</sub> (°)	θ <sub>2</sub> (°)	Cal. θ (°)	Exp. θ (°)
∠HC <sub>2</sub> O	2.0241	2.57707	3.9228	-16.88873	15	-13.61806	O	0.80561	0.79329 Eq. (15.150)	0.75	1	0.75	0.98470	0				117.02	115.9 (furan)
∠C <sub>2</sub> C <sub>3</sub> H <sub>4</sub>																117.02	110.69	117.02	
∠H <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	2.0241	2.66807	4.2269	-16.88873	15	-15.95954	C <sub>3</sub>	0.80561	0.85252	0.75	1	0.75	1.05822	0				128.09	128.0 (furan)
∠H <sub>2</sub> C <sub>2</sub> C <sub>3</sub>	2.0241	2.60925	4.2269	-16.88873	15	-15.95954	C <sub>3</sub>	0.80561	0.85252	0.75	1	0.75	1.05822	0				131.32	
∠H <sub>1</sub> C <sub>2</sub> C <sub>4</sub>	2.0241	2.60925	4.1312	-17.09334	18	-16.47951	C <sub>4</sub>	0.79597	0.82562	0.75	1	0.75	1.03725	0				125.76	
∠C <sub>2</sub> C <sub>3</sub> H <sub>4</sub>																125.76	107.01	127.23	128.0 (furan)
∠C <sub>2</sub> C <sub>3</sub> O	2.60925	2.57707	4.2661	-17.09334	18	-13.61806	O	0.79597	0.79329 Eq. (15.150)	1	1	1	0.79463	-1.65376				110.69	110.7 (furan)
∠C <sub>2</sub> OC <sub>3</sub>	2.57707	2.57707	4.1231	-18.22713	30	-18.22713	30	0.74646	0.74646	1	1	1	0.74646	-1.85836				106.25	106.6 (furan)
∠C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	2.60925	2.66807	4.2426	-17.81791	26	-18.02252	29	0.76360	0.75493	1	1	1	0.75927	-1.85836				107.01	106.1 (furan)



## THIOPHENE

Thiophene having the formula  $C_4H_4S$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the  $C-S-C$  functional group. The 1,3-butdiene moiety  
5 comprises  $C-C$ ,  $C=C$ , and  $CH$  functional groups. The  $CH$ ,  $C-C$ , and  $C=C$  groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The  $C-S-C$  functional group of thiophene is solved in a similar manner as that of the  $C-N-C$  group of pyrrole and the  $C-O-C$  group of furan. The solution of the  $C-S-C$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  
10  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the  $C-S-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron  
15 and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is  $c_2(\text{benzene } C2sp^3 HO) = 0.85252$  to match the double-bond character of the  $C2sp^3$  HOs, and the energy matching condition is further determined by the  $C_2$  parameter. Using the energy of  $S$ ,  $E(S) = -10.36001 \text{ eV}$  in Eq. (15.68) and the  $C2sp^3$  HO energy of  $E(C, 2sp^3) = -15.76868 \text{ eV}$  (Eq. (15.18) corresponding to  $s = 2$  in Eqs. (15.18-15.20), the  
20 hybridization factor  $C_2$  of Eq. (15.52) for the  $C-S-C$ -bond MO is

$$C_2(S3p \text{ to aryl-type } C2sp^3 HO) = \frac{E(S, 3p)}{E(C, 2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700 \quad (15.153)$$

$C_{1o}$  is also given by Eq. (15.153). Furthermore,  $\Delta E_{H_1 MO}(AO / HO)$  of the  $C-S-C$ -bond MO in Eq. (15.42) and  $E_r(\text{atom-atom, } msp^3.AO)$  in Eq. (15.52) are both  $-0.72457 \text{ eV}$  per atom corresponding to  $-2.89830 \text{ eV}$  in total. The energy contribution equivalent to that of  
25 a methyl group (Eq. (14.151)) and that of the  $C-S$ -bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the  $C2sp^3$  HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 67. The geometrical (Eqs. (15.1-15.5) and (15.42)),



intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.282 corresponding to functional-group composition of the molecule. The 5 bond angle parameters of thiophene determined using Eqs. (15.79-15.108) are given in Table 15.284.

Table 15.279. The symbols of functional groups of thiophene.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C = C$
$C_b - C_b$	$C - C$
$C_a - S - C_a$	$C - S - C$
CH	CH



Table 15.280. The geometrical bond parameters of thiophene and experimental values [1].

Parameter	C=C Group	C-C Group	C-S-C Group	CH Group
$a$ ( $a_0$ )	1.45103	1.77965	1.74058	1.53380
$c'$ ( $a_0$ )	1.30463	1.33404	1.62766	1.01120
Bond Length $2c'$ ( $\text{\AA}$ )	1.38076	1.41188	1.72264	1.07021
Exp. Bond Length ( $\text{\AA}$ )	1.370 (thiophene)	1.423 (thiophene)	1.714 (thiophene)	1.078 (thiophene)
$h_{sc}$ ( $a_0$ )	0.63517	1.17792	0.61671	1.15326
$e$	0.89910	0.74961	0.93513	0.65928

Table 15.281. The MO to HO intercept geometrical bond parameters of thiophene.  $R_i$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3, AO)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{\text{initial}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{bond}}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H$ ( $C, H$ )	$C_s$	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	84.49	95.51	44.74	1.08953	0.07833
$C-H$ ( $C, H$ )	$C'_s$	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_s = (H)C_s - C'_s(H) = C'_s$	$C'_s$	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_s = C'_s(H)(H)C'_s = C'_s$	$C'_s$	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$NC_s = C'_s(H)$	$C'_s$	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	137.14	42.86	60.85	0.70685	0.59777
$C'_s - C_s = C'_s(H)$	$C'_s$	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	141.52	38.48	55.36	0.98926	0.63840
$C'_s - C_s - C'_s = C'_s(H)$	$S$	-0.72457	-0.72457	0	0		1.37001	0.83600	-16.27490		142.17	37.83	56.24	0.96733	0.66033



Table 15.282. The energy parameters (eV) of functional groups of thiophene.

Parameters	C=C Group	C-C Group	C-S-C Group	CH Group
$n_1$	2	1	2	1
$n_2$	0	0	0	0
$n_3$	0	0	0	0
$c_1$	0.5	0.5	0.5	0.75
$c_2$	0.85252	1	0.65700	1
$c_3$	1	1	1	1
$c_4$	0.85252	0.85252	0.85252	0.91771
$c_5$	0	0	0	1
$c_6$	4	2	4	1
$c_7$	0	0	0	1
$c_{10}$	0.5	0.5	0.5	0.75
$c_{20}$	0.85252	1	0.65700	1
$V_c$ (eV)	-104.37986	-33.80733	-96.78916	-39.09538
$V_p$ (eV)	20.85777	10.19898	16.71820	13.45505
$T$ (eV)	35.96751	9.49831	27.80371	12.74462
$V_m$ (eV)	-17.98376	-4.74915	-13.90186	-6.37231
$E_{[10,10]}$ (eV)	0	-14.63489	0	-14.63489
$\Delta E_{H,10}$ (eV)	-2.26759	-1.85836	-2.89830	-2.26758
$E_{T,[10,10]}$ (eV)	2.26759	-12.77653	2.89830	-12.36731
$E_{T,[11,10]}$ (eV)	-63.27075	-31.63572	-63.27080	-31.63553
$E_T$ (atom-atom, $\text{mmp}^3$ , $AO$ ) (eV)	-2.26759	-2.26759	-2.89830	0
$E_{T,[10]}$ (eV)	-65.53833	-33.90295	-66.16903	-31.63537
$\omega$ ( $10^{15}$ rad/s)	15.4421	12.3131	10.3184	28.9084
$E_K$ (eV)	10.16428	8.10471	6.79173	19.02803
$E_P$ (eV)	-0.20668	-0.19095	-0.17058	-0.27301
$E_{K_{\text{orb}}}$ (eV)	0.17897	0.14829	0.08146	0.39427
	[6]	[48]	[41]	[56]
$E_{\text{res}}$ (eV)	-0.11720	-0.11680	-0.12985	-0.07587
$E_{\text{img}}$ (eV)	0.14803	0.14803	0.14803	0.14803
$E_T$ (comp) (eV)	-65.77272	-34.01976	-66.42873	-31.71124
$E_{\text{mold}}(E_{1,10,10})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{mold}}(E_{1,10,10})$ (eV)	0	0	0	-13.59844
$E_{T,1}$ (comp) (eV)	7.23317	4.74998	7.88917	3.32988



Table 15.283. The total bond energies of thiophene calculated using the functional group composition and the energies of Table 15.282 compared to the experimental values [2].

Name Formula	C=C		C-C		C-S-C		CH	
	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error					
C <sub>4</sub> H <sub>4</sub> S Thiophene	40.42501	40.430	0.00013					

Table 15.284. The bond angle parameters of thiophene and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom-atom, msp^3, AO)$ .

Atoms of Angle	2c' Bond 1 ( $\alpha_0$ )	2c' Bond 2 ( $\alpha_0$ )	2c' Terminal Atoms ( $\alpha_0$ )	$E_{\text{Condonable}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.B)	$E_{\text{Condonable}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	$c_2$ Atom 1 Eq. (15.63)	$c_2$ Atom 2 Eq. (15.126)	$C_1$	$C_2$	$c_1$	$c'_1$	$E_T$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_t$ ( $^\circ$ )	$\theta_s$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle HC_2S$	2.02241	3.25533	4.6030	-15.55033	3	-10.36001	S	0.87495 Eq. (15.63)	0.76144 Eq. (15.126)	0.75	0.76144 Eq. (15.126)	0.75	0.87495	0				119.58	119.9 (thiophene)
$\angle C_2C_3H_2$												119.58					119.58	115.84	124.58
$\angle H_2C_3C_4$	2.02241	2.68007	4.1633	-16.68412	14	-15.95954	6	0.81549	0.85252	0.75	1	0.75	1.04540	0				124.58	124.3 (thiophene)
$\angle H_2C_3C_4$	2.02241	2.60925	4.1633	-16.68412	14	-15.95954	6	0.81549	0.85252	0.75	1	0.75	1.04540	0				127.57	
$\angle H_2C_3C_4$	2.02241	2.60925	4.0825	-17.09334	18	-16.68412	14	0.79597	0.81549	0.75	1	0.75	1.02453	0				123.13	
$\angle C_2C_3H_2$																		123.13	124.3 (thiophene)
$\angle C_2C_3S$	2.60925	3.25533	4.9809	-17.81791	27	-10.36001	S	0.76360	0.65700 Eq. (15.153)	1	0.65700 Eq. (15.153)	1	0.71030	-0.72457		123.13	113.60	123.27	
$\angle C_3SC_4$	3.25533	3.25533	4.7958	-16.68412	14	-16.68412	14	0.81549	0.81549	1	1	1	0.81549	-1.85836				115.84	115.5 (thiophene)
$\angle C_3C_4C_2$	2.60925	2.66807	4.4159	-16.88873	15	-18.02252	29	0.80561	0.75493	1	1	1	0.78027	-1.85836				94.89	92.2 (thiophene)
																		113.60	112.5 (thiophene)



## IMIDAZOLE

Imidazole having the formula  $C_3H_4N_2$  comprises a conjugated system that is equivalent to pyrrole with one of the conjugated  $CH$  groups replaced by a nitrogen atom. The  $CH$ ,  $NH$ , and  $C=C$  groups are equivalent to the corresponding groups of pyrrole, 5 furan, and thiophene where present. In addition, the nitrogen substitution creates a  $C-N=C$  moiety comprising  $C-N$  and  $N=C$  functional groups. The  $C-N$  bonding is the same as that of a tertiary amine except that the hybridization term  $c_2$  in Eqs. (15.42) and (15.52) is that of the amino group of aniline,  $c_2(arylC2sp^3HO\ to\ N)=0.84665$  (Eq. (15.152)). The hybridization factor provides double-bond character to match the group to the 10 other orbitals of the molecule.  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\ eV$  (Eq. (14.513)). This matches the energy of the group to that of the contiguous  $N=C$  group wherein  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\ eV$  (Eq. (14.513)) per atom of the double bond with aromatic character as in the 15 case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene,  $n_1=2$  and  $C_2$  and  $C_{2v}$  are the same as  $C_2(benzeneC2sp^3HO)=0.85252$  (Eq. (15.143)) in Eqs. (15.42) and (15.52). To match the energy of the nitrogen to the  $C2sp^3\ HO$ ,  $c_2$  of the  $N=C$ -bond MO is also given by Eq. (15.152). These parameters also provide an energy match to the  $C-N-C$  group.

20 As in the case of pyrrole, the  $C-N-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1=2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ N)=0.84665$  (Eq. (15.152)) matches the double-bond character of the  $C2sp^3\ HOs$  to the  $N$  atom of the  $NH$  group, and  $C_2$  and  $C_{2v}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. 25 (15.143),  $C_2(benzeneC2sp^3HO)=0.85252$ . Furthermore,  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\ eV$  (Eq. (14.513)) per atom corresponding to  $-3.71673\ eV$  in total.



The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 68. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.79-15.108) are given in Table 15.290.

10 Table 15.285. The symbols of functional groups of imidazole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C = C$
$N_b = C_c$ double bond	$N = C$
$C_b - N_b$	$C - N$
$C_a - N_a - C_c$	$C - N - C$
$N_a H$ group	$NH$
CH	$CH$



Table 15.286. The geometrical bond parameters of imidazole and experimental values [1].

Parameter	C=C Group	N=C Group	C-N Group	C-N-C Group	NH Group	CH Group
$a$ ( $a_0$ )	1.45103	1.44926	1.82450	1.43222	1.24428	1.53380
$c'$ ( $a_0$ )	1.30463	1.30383	1.35074	1.29614	0.94134	1.01120
Bond Length $2c'$ ( $\text{\AA}$ )	1.38076	1.37991	1.42956	1.37178	0.996270	1.07021
Exp. Bond Length ( $\text{\AA}$ )	1.382 (pyrrole)			1.370 (pyrrole)	0.996 (pyrrole)	1.076 (pyrrole)
$h, c$ ( $a_0$ )	0.63517	0.63276	1.22650	0.60931	0.81370	1.15326
$e$	0.89910	0.89965	0.74033	0.90499	0.75653	0.65928

Table 15.287. The MO to HO intercept geometrical bond parameters of imidazole.  $R_i$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{insp}^3, \text{AO})$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{\text{bond}}$ ( $a_0$ )	$E_{\text{bond}}$ (eV) Final	$E(C'2sp^3)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C'-H$ ( $C', H$ )	$C'_a$	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.08931
$C'-H$ ( $C', H$ )	$C'_b$	-1.13380	-0.46459	0	0	-153.21408	0.91771	-16.42414	-16.23327	85.93	94.07	45.77	1.06995	0.03875
$C'-H$ ( $C', H$ )	$C'_c$	-0.92918	-0.92918	0	0	-153.47605	0.91771	-16.68411	-16.49325	84.49	95.51	44.47	1.08953	0.07833
$C'_a = (H)C'_b - N'_a = C'_c$	$C'_b$	-0.46459	-1.13380	0	0	-153.21408	0.91771	-16.42414	-16.23327	90.36	89.64	42.49	1.34547	0.00527
$C'_a = (H)C'_b - N'_a = C'_c$	$N'_a$	-0.46459	-0.92918	0	0		0.93084	-16.21953		91.32	88.68	43.14	1.33135	0.01939
$C'_a = (H)N'_a = C'_c$	$C'_a$	-1.13380	-0.46459	0	0	-153.21408	0.91771	-16.42414	-16.23327	137.64	42.36	61.49	0.69250	0.61213
$HN'_aC'_a = C'_b(H)$	$C'_c$	-1.13380	-0.92918	0	0	-153.67867	0.91771	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C'_b(H)N'_a - C'_a = C'_b(H)$	$C'_c$	-0.92918	-0.92918	0	0		0.91771	-16.88873	-16.69786	138.54	41.46	61.09	0.69238	0.60376
$C'_b(H)N'_a - C'_a = C'_b(H)$	$N'_a$	-0.92918	-0.92918	0	0		0.93084	-16.68411		138.92	41.08	61.59	0.68147	0.61467
$N'_a - H$ ( $N'_a, H$ )	$N'_a$	-0.92918	-0.92918	0	0		0.93084	-16.68411		117.34	62.66	62.90	0.36678	0.37456
$(H)C'_c - N'_aC'_a = C'_b(H)$	$C'_c$	-0.92918	-0.92918	0	0	-153.47605	0.91771	-16.68411	-16.49325	138.92	41.08	61.59	0.68147	0.61467
$C'_a = (H)C'_bN'_a = C'_c$	$C'_c$	-0.92918	-0.92918	0	0	-153.47605	0.91771	-16.68411	-16.49325	137.31	42.69	60.92	0.70446	0.59938
$C'_a = (H)C'_bN'_a = C'_c$	$N'_a$	-0.92918	-0.46459	0	0		0.93084	-16.21953		138.20	41.80	62.08	0.67849	0.62534



Table 15.288. The energy parameters (eV) of functional groups of imidazole.

Parameters	C=C Group	N=C Group	C-N Group	C-N-C Group	NH Group	CH Group
$n_1$	2	2	1	2	1	1
$n_2$	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0
$C_1$	0.5	0.5	0.5	0.5	0.75	0.75
$C_2$	0.85252	0.85252	1	0.85252	0.93613	1
$C_3$	1	1	1	1	0.75	1
$C_4$	0.85252	0.84665	0.84665	0.84665	0.92171	0.91771
$C_5$	0	0	0	0	1	1
$C_6$	4	4	2	4	1	1
$C_7$	0	0	0	0	1	1
$C_8$	0.5	0.5	0.5	0.5	0.75	0.75
$C_{10}$	0.85252	0.85252	1	0.85252	1	1
$V_1$ (eV)	-104.37986	-103.92756	-32.44864	-106.58684	-39.48897	-39.09538
$V_2$ (eV)	20.85777	20.87050	10.07285	20.99432	14.45367	13.45505
$T$ (eV)	35.96751	35.85539	8.89248	37.21047	15.86820	12.74462
$V_3$ (eV)	-17.98376	-17.92770	-4.44624	-18.60523	-7.93410	-6.37231
$E_1$ (eV)	0	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_{1,2}}$ (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	-2.26758
$E_2$ (eV)	2.26759	1.85836	-13.70571	3.71673	-14.53414	-12.36731
$E_3$ (eV)	-63.27075	-63.27100	-31.63527	-63.27056	-31.63534	-31.63533
$E_4$ (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	0
$E_5$ (eV)	-65.53833	-65.12910	-32.56455	-66.98746	-31.63537	-31.63537
$\omega$ ( $10^6$ rad/s)	15.4421	15.4704	21.5213	15.7474	48.7771	28.9084
$E_6$ (eV)	10.16428	10.18290	14.16571	10.36521	32.10594	19.02803
$E_7$ (eV)	-0.20668	-0.20558	-0.24248	-0.21333	-0.35462	-0.27301
$E_8$ (eV)	0.17897	0.20768	0.12944	0.11159	0.40696	0.39427
$E_9$ (eV)	-0.11720	-0.10174	-0.17775	-0.15754	-0.15115	-0.07587
$E_{10}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{11}$ (eV)	-65.77272	-65.33259	-32.74230	-67.30254	-31.78651	-31.71124
$E_{12}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{13}$ (eV)	0	0	0	0	-13.59844	-13.59844
$E_{14}$ (eV)	7.23317	6.79303	3.47253	8.76298	3.51208	3.32988



Table 15.289. The total bond energies of imidazole calculated using the functional group composition and the energies of Table 15.288 compared to the experimental values [2].

Formula	Name	$C=C$	$N=C$	$C-N$	$C-N-C$	NH	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_4N_2$	Imidazole	1	1	1	1	1	3	39.74106	39.74106	-0.00056

Table 15.290. The bond angle parameters of imidazole and experimental values [59]. In the calculation of  $\theta_{\alpha}$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, nsp, AO)$ .

Atom of Angle	$2C_1$ Bond 1 ( $\alpha_1$ )	$2C_1$ Bond 2 ( $\alpha_2$ )	$2C_1$ Terminal Atoms ( $\alpha_3$ )	$E_{\alpha}$ value for Atom 1	Atom 1 Hybridization Designation (Table 15.33)	$E_{\alpha}$ value for Atom 2	Atom 2 Hybridization Designation (Table 15.33)	$C_1$	$C_2$	$C_1 - C_2$	$\zeta_1$	$E_T$ (eV)	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle HC-N_a$	2.02241	2.59228	4.0166	-14.82575	1	-14.53414	N	0.91771	0.92171 (Eq. (15.151))	1	0.75	1.00435	0	120.51	120.51	117.4 (imidazole)
$\angle C-C-H_a$													120.51	106.63	132.86	136.3 (imidazole)
$\angle HN-C_a$	1.88268	2.59228	3.8987	-14.53414	N	-16.49225	13	0.84665 (Eq. (15.151))	0.82493 (Eq. (15.64))	1	0.75	0.97435	0	120.37	120.37	127.9 (imidazole)
$\angle H-C-C_a$	2.02241	2.60925	4.3895	-16.88873	15	-15.75493	4	0.80561	0.86359	1	0.75	1.07196	0	135.30	135.30	136.3 (imidazole)
$\angle H-C-C_a$	2.02241	2.60925	4.2740	-15.95954	6	-14.82575	1	0.85252	0.91771	1	0.75	1.07647	0	134.28	134.28	133.2 (imidazole)
$\angle N-C-H_a$													134.28	111.18	114.54	115.8 (imidazole)
$\angle H-C-N_a$	2.02241	2.59228	3.8471	-15.95954	6	-14.53414	N	0.87495	0.84665 (Eq. (15.152))	1	0.75	0.96765		112.37	112.37	110.4 (imidazole)
$\angle N-C-H_e$													112.37	109.83	137.80	138.2 (imidazole)
$\angle HN-C_e$	1.88268	2.59228	4.0661	-14.53414	N	-15.76668	6	0.84665 (Eq. (15.151))	0.86284 (Eq. (15.64))	1	0.75	1.01912	0	129.96	129.96	129.1 (imidazole)
$\angle N-C-C_a$	2.59228	2.60925	4.1952	-14.53414	N	-17.09334	18	0.84665 (Eq. (15.152))	0.79597	1	1	0.82131	-1.44915	107.52	107.52	106.3 (imidazole)
$\angle C-N-C_e$	2.59228	2.59228	4.2426	-17.81791	26	-17.81791	26	0.76360	0.76360	1	1	0.76360	-1.85836	109.83	109.83	107.2 (imidazole)
$\angle C-N-C_a$	2.60766	2.70148	4.3128	-17.61330	23	-17.61330	25	0.77247	0.77247	1	1	0.77247	-1.85836	108.64	108.64	105.4 (imidazole)
$\angle C-C-N_a$	2.60925	2.70148	4.3818	-15.95955	6	-14.53414	N	0.85222 (Eq. (15.152))	0.84665 (Eq. (15.152))	1	1	0.84958	-1.85836	111.18	111.18	109.8 (imidazole)
$\angle N-C-N_a$	2.59228	2.60766	4.2544	-16.68411	13	-16.21953	8	0.81549	0.83885	1	1	0.82717	-1.44915	109.80	109.80	111.3 (imidazole)



## PYRIDINE

Pyridine has the formula  $C_5H_5N$  and comprises the benzene molecule with one  $CH$  group replaced by a nitrogen atom which gives rise to a  $C=N$  functional group. The aromatic  $C=C$  and  $C-H$  functional groups are equivalent to those of benzene given in the 5 Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the  $C=N$  group which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine  $C2sp^3$  HO initially has four unpaired electrons. Each  $C-H$  bond has two paired electrons with one donated from the  $H$  AO and the other from the  $C2sp^3$  HO. In pyridine the three  $N2p$  electrons are 10 donated to the aromatic bond. Thus, as in the case of the  $C=C$  group, each  $C=N$  bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the  $C2sp^3$  HO and the  $N2p$  AO of the participating carbon and nitrogen atoms, respectively.

The solution of the  $C=N$  functional group comprises the hybridization of the  $2s$  and 15  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The  $C=N$ -bond MO is solved as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.147). The hybridization factor  $c_2(C2sp^3HO \text{ to } N) = 0.91140$  (Eq. (15.116)) matches the double-bond character of the 20  $C2sp^3$  HO to the  $N$  atom, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.147) are also given by Eq. (15.116) in order to match the nitrogen to the aromatic  $C2sp^3$  HO such that  $\Delta E_{H_2MO}(AO/HO) = 0$  in Eq. (15.42). Furthermore,  $E_r(atom - atom, msp^3.AO)$  of the  $C=N$ -bond MO in Eq. (15.147) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.44915 \text{ eV}$  corresponding to an energy contribution from each atom that is 25 equivalent to that of an independent methyl group,  $-0.72457 \text{ eV}$  (Eq. (14.151)). The contributions are also the same as those for a primary amine group as given in the corresponding section. As in the case of benzene, the aromatic  $E_r(Group)$  and  $E_D(Group)$  are



given by Eqs. (15.146) and (15.147), respectively, with  $f_1 = 0.75$ . The breakage of the *CNC* bonds results in three unpaired electrons on the *N* atom. Thus, the corresponding  $E_{mag}$  given by Eq. (15.60) was normalized for the two bonds per atom and for  $f_1 = 0.75$  and was subtracted from the total energy of the  $C \overset{3e}{=} N$ -bond MO in Eq. (15.147). The pyridine vibrational energies are similar to those of benzene [60]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each  $E_D(\text{group})$  of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.79-15.108) are given in Table 15.296.

Table 15.291. The symbols of functional groups of pyridine.

Functional Group	Group Symbol
CC (aromatic bond)	$C \overset{3e}{=} C$
CH (aromatic)	$CH$
$C_a \overset{3e}{=} N$	$C \overset{3e}{=} N$



Table 15.292. The geometrical bond parameters of pyridine and experimental values [1].

Parameter	C=C Group	C-H Group	C=N Group
$a(a_0)$	1.47348	1.60061	1.47169
$c'(a_0)$	1.31468	1.03299	1.27073
Bond Length $2c'(A)$	1.39140	1.09327	1.34489
Exp. Bond Length (A)	1.394 (pyridine)	1.084 (pyridine)	1.340 (pyridine)
$b_0 c'(a_0)$	0.66540	1.22265	0.74237
$e$	0.89223	0.64537	0.86345

Table 15.293. The MO to HOMO intercept geometrical bond parameters of pyridine.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C'2_{sp}$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{total}}(C'2_{sp})$ (eV) Final	$\bar{E}(C'2_{sp})$ (eV) Final	$\theta^*$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H(C'H)$	$C'$	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H(C'H)$	$C'$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09314	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$(H)C'_s(H)C'_s=NC'_s$	$C'_s$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$(H)C'_s(H)C'_s=NC'_s$	$N$	-0.54343	-0.54343	0	0		0.93084	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$(H)C'_s=NC'_s(H)N$	$C'_s$	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)C'_s=NC'_s(H)N$	$C'_s$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09314	-16.90248	134.24	45.76	58.98	0.75915	0.55533



Table 15.294. The energy parameters (eV) of functional groups of pyridine.

Parameters	C=C Group	C-H Group	C=N Group
$f_1$	0.75	1	0.75
$n_1$	2	1	2
$n_2$	0	0	0
$n_3$	0	0	0
$c_1$	0.5	0.75	0.5
$c_2$	0.85252	1	0.91140
$c_3$	1	1	1
$c_4$	0.85252	0.91771	0.91140
$c_5$	0	1	0
$c_6$	3	1	3
$c_7$	0	1	0
$c_8$	0.5	0.75	0.5
$c_9$	0.85252	1	0.91140
$V_1$ (eV)	-101.12679	-37.10024	-102.01431
$V_2$ (eV)	20.69825	13.17125	21.41410
$T$ (eV)	34.31559	11.58941	34.65890
$V_m$ (eV)	-17.15779	-5.79470	-17.32945
$E_1$ (eV)	0	-14.63489	0
$\Delta E_{10,100}$ (eV)	0	-1.13379	0
$E_2$ (eV)	0	-13.50110	0
$E_3$ (eV)	-63.27075	-31.63539	-63.27076
$E_4$ (eV)	-2.26759	-0.56690	-1.44915
$E_5$ (eV)	-65.53833	-32.20226	-64.71988
$\omega$ ( $10^5$ rad/s)	49.7272	26.4826	43.6311
$E_6$ (eV)	32.73133	17.43132	28.71875
$E_7$ (eV)	-0.35806	-0.26130	-0.33540
$E_8$ (eV)	0.19649	0.35532	0.19649
$E_9$ (eV)	[49]	Eq. (13.458)	[49]
$E_{10}$ (eV)	-0.25982	-0.08364	-0.23715
$E_{11}$ (eV)	0.14803	0.14803	0.09457
$E_{12}$ (eV)	-49.54347	-32.28590	-48.82472
$E_{13}$ (eV)	-14.63489	-14.63489	-14.63489
$E_{14}$ (eV)	0	-13.59844	0
$E_{15}$ (eV)	5.63881	3.90454	4.92005



Table 15.295. The total bond energies of pyridine calculated using the functional group composition and the energies of Table 15.294 compared to the experimental values [2].

Formula	Name	$C \equiv C$	$C^{\equiv}H$	$C \equiv N$	Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_5H_5N$	Pyridine	4	5	2		51.91802	51.87927	-0.00075

Table 15.296. The bond angle parameters of pyridine and experimental values [1].  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

Atoms of Angle	$2c'$ Bond 1 ( $a_s$ )	$2c'$ Bond 2 ( $a_s$ )	$2c'$ Terminal Atoms ( $a_s$ )	$F_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$F_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c_2'$	$E_T$ (eV)	$\theta_v$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C' C' C'$ (aromatic)	2.6936	2.6936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle C' C' H$ (aromatic)																		119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle H C' N$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771 Eq (15.116)	0.9140 Eq (15.116)	0.75	1	0.75	0.99312	0				117.65	115.9 (pyridine)
$\angle N C' C'_s$	2.54147	2.6936	4.5607	-14.53414	N	-16.52644 $C'_s$	12	0.9140 Eq (15.116)	0.82327	1	1	1	0.86734	-1.44915				123.76	123.9 (pyridine)
$\angle C' N C'_s$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	0.76801	-1.85836				117.09	116.8 (pyridine)



## PYRIMIDINE

Pyrimidine has the formula  $C_4H_4N_2$  and comprises the pyridine molecule with one additional  $CH$  group replaced by a nitrogen atom which gives rise to a second  $C^{3e}=N$  functional group that is equivalent to that of pyridine given in the corresponding section. The aromatic  $C^{3e}=C$  and  $C-H$  functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the  $C^{3e}=N$  group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 70. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each  $E_D(\text{group})$  of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.79-15.108) are given in Table 15.302.

Table 15.297. The symbols of functional groups of pyrimidine.

Functional Group	Group Symbol
$CC$ (aromatic bond)	$C^{3e}=C$
$CH$ (aromatic)	$CH$
$C_{a,b,a}^{3e}=N$	$C^{3e}=N$



Table 15.298. The geometrical bond parameters of pyrimidine and experimental values [1].

Parameter	C=C Group	C <sup>≡</sup> N Group	C <sup>≡</sup> N Group
$a$ ( $a_0$ )	1.47348	1.60061	1.47169
$c'$ ( $a_0$ )	1.31468	1.03299	1.27073
Bond Length $2c'$ ( $\text{\AA}$ )	1.39140	1.09327	1.34489
Exp. Bond Length ( $\text{\AA}$ )	1.393 (pyrimidine)	1.084 (pyrimidine)	1.340 (pyrimidine)
$b, c$ ( $a_0$ )	0.66540	1.22265	0.74237
$v$	0.89223	0.64537	0.86345

Table I5.299. The MO to HO intercept geometrical bond parameters of pyrimidine.  $E_T$  is  $E_T(\text{atom} \rightarrow \text{atom}, \text{misp}^3, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C_{2,sp^3}$ (eV)	$r_{final}$ ( $a_0$ )	$r_{final}$ ( $a_0$ )	$E_{Coulomb}$ ( $C_{2,sp^3}$ ) (eV) Final	$E(C_{2,sp^3})$ (eV) Final	$\theta^*$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H(C_uH)$	$C_u$	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.38864	78.27	101.73	41.39	1.20084	0.16785
$C-H(C_{s_u}H)$	$C_s$ $C_d$	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H(C_iH)$	$C_i$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21979
$(H)C_i(H)C_uN_u=C_uC_u$ $(H)C_i(H)C_d=N_uC_u$	$C_s$ $C_d$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$(H)C_i(H)C_s=N_uC_u$ $(H)C_i(H)C_d=N_uC_u$	$N_u$ $N_u$	-0.54343	-0.54343	0	0	-153.26945	0.93084	0.85503	-15.91261	-16.28865	130.61	49.39	60.97	0.71418	0.55656
$(H)C_i(H)C_uN_u=C_i(H)$ $(H)C_i(H)C_dN_u=C_i(H)$	$C_u$	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	129.26	50.74	59.44	0.74824	0.52249
$(H)C_i(H)C_uN_u=C_i(H)$ $(H)C_i(H)C_dN_u=C_i(H)$	$N_u$ $N_u$	-0.54343	-0.54343	0	0	-153.26945	0.93084	0.85503	-15.91261	-16.28865	130.61	49.39	60.97	0.71418	0.55656
$N_u(H)C_u=C_i(H)C_u$ $N_u(H)C_s=C_i(H)C_d$	$C_i$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$N_u(H)C_u=C_i(H)C_u$ $N_u(H)C_s=C_i(H)C_d$	$C_s$ $C_d$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165



Table 15.300. The energy parameters (eV) of functional groups of pyrimidine.

Parameters	$\overset{\text{H}}{\underset{\text{C}}{\text{C}}}$ Group	$\overset{\text{H}}{\underset{\text{C}}{\text{N}}}$ Group	$\overset{\text{H}}{\underset{\text{C}}{\text{N}}}$ Group
$f_1$	0.75	1	0.75
$n_1$	2	1	2
$n_2$	0	0	0
$n_3$	0	0	0
$C_1$	0.5	0.75	0.5
$C_2$	0.85252	1	0.91140
$c_1$	1	1	1
$c_2$	0.85252	0.91771	0.91140
$c_3$	0	1	0
$c_4$	3	1	3
$c_5$	0	1	0
$C_{10}$	0.5	0.75	0.5
$C_{10}$	0.85252	1	0.91140
$V_e$ (eV)	-101.12679	-37.10024	-102.01431
$V_p$ (eV)	20.69825	13.17125	21.41410
$T$ (eV)	34.31559	11.58941	34.65890
$V_m$ (eV)	-17.15779	-5.79470	-17.32945
$E_{100}$ (eV)	0	-14.63489	0
$\Delta E_{H_{250}}$ (eV)	0	-1.13379	0
$E_{100}$ (eV)	0	-13.50110	0
$E_{100}$ (eV)	-63.27075	-31.63539	-63.27076
$E_{100}$ (eV)	-2.26759	-0.56690	-1.44915
$E_{100}$ (eV)	-65.53833	-32.20226	-64.71988
$\omega$ ( $10^5$ rad/s)	49.7272	26.4826	43.6311
$E_p$ (eV)	32.73133	17.43132	28.71875
$E_p$ (eV)	-0.35806	-0.26130	-0.35540
$E_{100}$ (eV)	0.19649	0.35532	0.19649
$E_{100}$ (eV)	[49]	Eq. (13.458)	[49]
$E_{100}$ (eV)	-0.25982	-0.08364	-0.23715
$E_{100}$ (eV)	0.14803	0.14803	0.09457
$E_{100}$ (eV)	-49.54347	-32.28590	-48.82472
$E_{100}$ (eV)	-14.63489	-14.63489	-14.63489
$E_{100}$ (eV)	0	-13.59844	0
$E_{100}$ (eV)	5.63881	3.90454	4.92005



Table 15.301. The total bond energies of pyrimidine calculated using the functional group composition and the energies of Table 15.300 compared to the experimental values [2].

Formula	Name	$\overset{+}{C}=\overset{+}{C}$	$\overset{+}{C}-H$	$\overset{+}{C}-N$	Group	Calculated Total Bond Energy (eV)	Experiment Total Bond Energy (eV)	Relative Error
$C_4H_4N_2$	Pyrimidine	2	4	4	4	46.5797	46.5794	-0.00125

Table 15.302. The bond angle parameters of pyrimidine and experimental values [1].  $E_r$  is  $E_r(amin - amin, nsp^3 AO)$ .

Atoms of Angle	$\angle C^1$ Bond 1 ( $\alpha_1$ )	$\angle C^1$ Bond 2 ( $\alpha_2$ )	$\angle C^1$ Terminal Atom ( $\alpha_0$ )	$E_r$ calculated Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_r$ calculated Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	$C_2$ Atom 1	$C_2$ Atom 2	$C_1$	$C_2$	$C_1$	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$\theta_3$ ( $^\circ$ )	$E_r$ (eV)	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle(C^1C^1)$ (aromatic)	2.62936	2.62936	4.5385	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1				-1.85836	120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle(C^1H)$ (aromatic)													120.19				119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle HCN$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 $E_{\alpha}$ (15.116)	0.75	1	0.75				0	117.65	115.9 (pyridine)
$\angle NC^1$	2.54147	2.62936	4.5607	-14.53414	N	-16.52644	13	0.91140 $E_{\alpha}$ (15.116)	0.82327	1	1	1				-1.44915	123.76	121.9 (pyridine)
$\angle C^1NC^1$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1				-1.85836	117.09	115.5 (pyrimidine)
$\angle NC^1N$	2.54147	2.54147	4.5826	-15.55033	3	-15.55033	3	0.87495	0.87495	1	1	1				-1.85836	128.73	127.6 (pyrimidine)



## PYRAZINE

Pyrazine has the formula  $C_4H_4N_2$  and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The  $C \overset{3e}{=} N$  functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic  $C \overset{3e}{=} C$  and  $C-H$  functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the  $C \overset{3e}{=} N$  group which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 71. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrazine determined using Eqs. (15.79-15.108) are given in Table 15.308.

Table 15.303. The symbols of functional groups of pyrazine.

Functional Group	Group Symbol
CC (aromatic bond)	$C \overset{3e}{=} C$
CH (aromatic)	$CH$
$C \overset{3e}{=} N$	$C \overset{3e}{=} N$



Table 15.304. The geometrical bond parameters of pyrazine and experimental values [1].

Parameter	$C \equiv C$ Group	$CH$ Group	$C=N$ Group
$a$ ( $a_0$ )	1.47348	1.60061	1.47169
$c'$ ( $a_0$ )	1.31468	1.03299	1.27073
Bond Length $2c'$ ( $\text{\AA}$ )	1.39140	1.09327	1.34489
Exp. Bond Length ( $\text{\AA}$ )	1.339 (pyrazine)	1.115 (pyrazine)	1.403 (pyrazine)
$h_1 c'$ ( $a_0$ )	0.66540	1.22265	0.74237
$u$	0.89223	0.64537	0.86345

Table 15.305. The MO to HO intercept geometrical bond parameters of pyrazine.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{usp}^3, AO)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy C2sp <sup>3</sup> (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{intercept}}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H(C_{\text{H}})$	$C_{\text{H}}$	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$(H)C_{\text{H}}(H)C_{\text{H}}=NC_{\text{H}}$	$C_{\text{H}}$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50801
$(H)C_{\text{H}}(H)C_{\text{H}}=NC_{\text{H}}$	N	-0.54343	-0.54343	0	0		0.93084	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$N(H)C_{\text{H}}=C_{\text{H}}(H)N$	$C_{\text{H}}$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165



Table 15.306. The energy parameters (eV) of functional groups of pyrazine.

Parameters	C=C Group	CH Group	C=N Group
$f_1$	0.75	1	0.75
$n_1$	2	1	2
$n_2$	0	0	0
$n_3$	0	0	0
$C_1$	0.5	0.75	0.5
$C_2$	0.85252	1	0.91140
$c_1$	1	1	1
$c_2$	0.85252	0.91771	0.91140
$c_3$	0	1	0
$c_4$	3	1	3
$c_5$	0	1	0
$C_{10}$	0.5	0.75	0.5
$C_{20}$	0.85252	1	0.91140
$V_e$ (eV)	-101.12679	-37.10024	-102.01431
$V_p$ (eV)	20.69825	13.17125	21.41410
$T$ (eV)	34.31559	11.58941	34.65890
$V_n$ (eV)	-17.15779	-5.79470	-17.32945
$E(\pi\pi^*)$ (eV)	0	-14.63489	0
$\Delta E_{HOMO}$ (eV)	0	-1.13379	0
$E_T(\pi\pi^*)$ (eV)	0	-13.50110	0
$E_T(\pi\pi^*)$ (eV)	-63.27075	-31.63539	-63.27076
$E_T(\pi\pi^*)$ (eV)	-2.26759	-0.56690	-1.44915
$E_T(\pi\pi^*)$ (eV)	-65.53833	-32.20226	-64.71988
$\omega$ ( $10^5$ rad/s)	49.7272	26.4826	43.6311
$E_p$ (eV)	32.73133	17.43132	28.71875
$E_p$ (eV)	-0.35806	-0.26130	-0.33540
$E_{\text{HOMO}}$ (eV)	0.19649	0.35532	0.19649
$E_{\text{HOMO}}$ (eV)	[49]	Eq. (13.458)	[49]
$E_{\text{HOMO}}$ (eV)	-0.25982	-0.08364	-0.23715
$E_{\text{HOMO}}$ (eV)	0.14803	0.14803	0.09457
$E_T(\pi\pi^*)$ (eV)	-49.54347	-32.28590	-48.82472
$E_{\text{HOMO}}$ (eV)	-14.63489	-14.63489	-14.63489
$E_{\text{HOMO}}$ (eV)	0	-13.59844	0
$E_{\text{HOMO}}$ (eV)	5.63881	3.90454	4.92005



Table 15.307. The total bond energies of pyrazine calculated using the functional group composition and the energies of Table 15.306 compared to the experimental values [2].

Formula	Name	$\sum C \equiv C$	$\sum C-H$	$\sum C=N$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_4N_2$	Pyrazine	2	4	4	46.57397	46.51380	0.00095

Table 15.308. The bond angle parameters of pyrazine and experimental values [1].  $E_T$  is  $E_T(atom - atom, exp, AO)$ .

Atoms of Angle	$2c'$ Bond 1 ( $a_0$ )	$2c'$ Bond 2 ( $a_0$ )	$2c'$ Terminal Atoms ( $a_0$ )	$E_{T,calc}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{T,calc}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c'_1$	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232			120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle CCH$ (aromatic)														120.19		119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle HCN$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116)	0.75	1	0.75	0.99312			117.65	115.9 (pyridine)
$\angle CCH$														117.65	116.81	125.54	123.9 (pyridine)
$\angle NCC$	2.54147	2.62936	4.4045	-14.53414	N	-17.09334	7	0.91140 Eq. (15.116)	0.79597	1	1	1	0.85368			116.81	115.6 (pyrazine)
$\angle CNC$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	0.76801			117.09	116.8 (pyrimidine)



## QUINOLINE

Quinoline has the formula  $C_9H_7N$  and comprises the naphthalene molecule with one  $CH$  group replaced by a nitrogen atom which gives rise to a  $C=N^{3e}$  functional group. The aromatic  $C=C^{3e}$  and  $C-H$  functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the  $C=N^{3e}$  group which is also aromatic. The  $C-C$  functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the  $C=N^{3e}$  group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 72. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.79-15.108) are given in Table 15.314.

Table 15.309. The symbols of functional groups of quinoline.

Functional Group	Group Symbol
$CC$ (aromatic bond)	$C=C^{3e}$
$CH$ (aromatic)	$CH$
$C_h - C_h$ (bridging bond)	$C - C$
$C_{a,d}^{3e} = N$	$C=N^{3e}$



Table 15.31.0. The geometrical bond parameters of quinoline and experimental values [1].

Parameter	$C=C$ Group	$CH$ Group	$C-C$ Group	$C=N$ Group
$a$ ( $a_0$ )	1.47348	1.60061	1.75607	1.47169
$c'$ ( $a_0$ )	1.31468	1.03299	1.32517	1.27073
Bond Length $2c'$ ( $\text{\AA}$ )	1.39140	1.09327	1.40250	1.34489
Exp. Bond Length ( $\text{\AA}$ )	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
$b,c$ ( $a_0$ )	0.66540	1.22265	1.15226	0.74237
$e$	0.89223	0.64537	0.75462	0.86345

Table 15.31.1. The MO to HO intercept geometrical bond parameters of quinoline.  $E_T$  is  $E_T(atom - atom, msp^3 AO)$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C2_{sp^3}$ (eV)	$r_{final}$ ( $a_0$ )	$E_{C_{2sp^3}}$ (eV) Final	$E(C2_{sp^3})$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	$d_1$ ( $a_0$ )	$d_2$ ( $a_0$ )
$C-H$ ( $C_uH$ )	$C_u$	-0.85035	-0.54343	-0.56690	0	-153.57656	0.91771	-16.78642	-16.59556	76.35	103.65	40.11	1.23423	0.19124
$C-H$ ( $C_uH$ )	$C_u$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$N(H)C_u=C_u(H)$	$C_u$	-0.85035	-0.54343	-0.56690	0	-153.57656	0.91771	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)C_u=C_u(H)$	$C_u$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$(H)C_u(C_u)C_u=C_u$	$C_u$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57038
$N(C_u)C_u=C_u$	$C_u$	-0.85035	-0.54343	-0.28345	0	-153.29292	0.91771	-16.50298	-16.31211	135.42	44.58	60.42	0.72743	0.58725
$C_u(H)C_u=N$	$C_u$	-0.85035	-0.54343	-0.56690	0	-153.57656	0.91771	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50801
$C_u(H)C_u=N$	$N$	-0.54343	-0.54343	0	0		0.93084	-15.91561		130.61	49.39	60.97	0.71418	0.55656
$C_u(C_u)C_u=N$	$C_u$	-0.85035	-0.54343	-0.28345	0	-153.29291	0.91771	-16.50297	-16.31211	128.21	50.79	59.38	0.74960	0.52113
$(H)C_u=C_u(C_u)C_u$	$C_u$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	-16.80989	-16.61903	95.01	84.99	44.41	1.25451	0.07066
$N(C_u)C_u=C_u$	$C_u$	-0.85035	-0.54343	-0.28345	0	-153.29292	0.91771	-16.50298	-16.31211	96.31	83.69	45.33	1.23456	0.09061



Table 15.312. The energy parameters (eV) of functional groups of quinoline.

Parameters	C=C Group	CH Group	C-C Group	C=N Group
$f_1$	0.75	1	1	0.75
$n_1$	2	1	1	2
$n_2$	0	0	0	0
$n_3$	0	0	0	0
$C_1$	0.5	0.75	0.5	0.5
$C_2$	0.85252	1	1	0.91140
$C_3$	1	1	1	1
$C_4$	0.85252	0.91771	0.85252	0.91140
$C_5$	0	1	0	0
$C_6$	3	1	2	3
$C_7$	0	1	0	0
$C_{10}$	0.5	0.75	0.5	0.5
$C_{10}$	0.85252	1	1	0.91140
$V_c$ (eV)	-101.12679	-37.10024	-34.43791	-102.01431
$V_r$ (eV)	20.69825	13.17125	10.26723	21.41410
$T$ (eV)	34.31559	11.58941	9.80539	34.65890
$V_m$ (eV)	-17.15779	-5.79470	-4.90270	-17.32945
$E_{\text{HOMO}}$ (eV)	0	-14.63489	-14.63489	0
$\Delta E_{\text{HOMO}}$ (eV)	0	-1.13379	-1.13379	0
$E_{\text{HOMO}}$ (eV)	0	-13.50110	-13.50110	0
$E_{\text{HOMO}}$ (eV)	-63.27075	-31.63539	-31.63539	-63.27076
$E_{\text{HOMO}}$ (eV)	-2.26759	-0.56690	-0.56690	-1.44915
$E_{\text{HOMO}}$ (eV)	-65.53833	-32.20226	-32.20226	-64.71988
$\omega$ ( $10^5$ rad/s)	49.7272	26.4826	23.6343	43.6311
$E_{\text{HOMO}}$ (eV)	32.73133	17.43132	15.55648	28.71875
$E_{\text{HOMO}}$ (eV)	-0.33806	-0.26130	-0.25127	-0.33540
$E_{\text{HOMO}}$ (eV)	0.19649	0.35532	0.12312	0.19649
$E_{\text{HOMO}}$ (eV)	[49]	$E_0$ (13.438)	[2]	[49]
$E_{\text{HOMO}}$ (eV)	-0.25982	-0.08364	-0.18971	-0.23715
$E_{\text{HOMO}}$ (eV)	0.14803	0.14803	0.14803	0.09457
$E_{\text{HOMO}}$ (eV)	49.54347	-32.28590	-32.39198	-48.82472
$E_{\text{HOMO}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{HOMO}}$ (eV)	0	-13.59844	0	0
$E_{\text{HOMO}}$ (eV)	5.63881	3.90454	3.12220	4.92005



Table 15.313. The total bond energies of quinoline calculated using the functional group composition and the energies of Table 15.312 compared to the experimental values [2].

Formula	Name	<sup>3s</sup> C≡C	<sup>3s</sup> C-C	<sup>3s</sup> C=N	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>6</sub> H <sub>6</sub> N	Quinoline	8	1	2	85.40453	85.48607	0.00178

Table 15.314. The bond angle parameters of quinoline and experimental values [1].  $E_T$  is  $E_T(\text{atom} \sim \text{atom}, \text{msp}^3 \cdot \text{AO})$ .

Atoms of Angle	$2c'_1$ Bond 1 ( $a_1$ )	$2c'_2$ Bond 2 ( $a_2$ )	$2c'_3$ Terminal ( $a_3$ )	$E_{\text{calculated}}$ Atom 1 ( $a_1$ )	Atom 1 Hybridization Designation (Table 15.3B)	$E_{\text{calculated}}$ Atom 2 Hybridization Designation (Table 15.3B)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c'_1$	$c'_2$	$E_r$ (eV)	$\theta_v$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$ZCC$	2.62936	2.65034	4.5383	-17.17218	20	-17.17218	0.79222	0.79232	1	1	1	0.79232	-1.85336				119.40	119.4
$ZCH$																	120.30	
$ZC,NC$	2.56147	2.56147	4.3818	-17.03216	22	-17.71560	0.78050	0.76801	1	1	1	0.77406	-1.85336		119.40		119.10	(naphthalene)



## ISOQUINOLINE

Isoquinoline has the formula  $C_9H_7N$  and comprises the naphthalene molecule with one  $CH$  group replaced by a nitrogen atom which gives rise to a  $C \overset{3e}{=} N$  functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic  $C \overset{3e}{=} C$  and  $C-H$  functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the  $C \overset{3e}{=} N$  group which is also aromatic. The  $C-C$  functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the  $C \overset{3e}{=} N$  group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 73. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of isoquinoline are given in Tables 15.316, 15.317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.79-15.108) are given in Table 15.320.

Table 15.315. The symbols of functional groups of isoquinoline.

Functional Group	Group Symbol
$CC$ (aromatic bond)	$C \overset{3e}{=} C$
$CH$ (aromatic)	$CH$
$C_b - C_b$ (bridging bond)	$C - C$
$C_{a,d} \overset{3e}{=} N$	$C \overset{3e}{=} N$



Table 15.316. The geometrical bond parameters of isoquinoline and experimental values [1].

Parameter	C=C Group	CH Group	C-C Group	C=N Group
$a$ ( $a_0$ )	1.47348	1.60061	1.75607	1.47169
$c'$ ( $a_0$ )	1.31468	1.03299	1.32517	1.27073
Bond Length $2c'$ ( $\text{\AA}$ )	1.39140	1.09327	1.40250	1.34489
Exp. Bond Length ( $\text{\AA}$ )	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
$h, c$ ( $a_0$ )	0.66540	1.22265	1.15226	0.74237
$c$	0.89223	0.64537	0.75462	0.86345

Table 15.317. The MO to HO intercept geometrical bond parameters of isoquinoline.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{resp. } \Delta O)$ .

Bond	Atom	$E_r$ (eV) Bond 1	$E_r$ (eV) Bond 2	$E_r$ (eV) Bond 3	$E_r$ (eV) Bond 4	Final Total Energy $C_{2sp^3}$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{total}}(C_{2sp^3})$ (eV) Final	$\theta'$ ( $^\circ$ )	$\theta_i$ ( $^\circ$ )	$\theta_j$ ( $^\circ$ )	$d_i$ ( $a_0$ )	$d_j$ ( $a_0$ )
C-H ( $C_a H$ )	$C_a$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	76.35	103.65	40.11	1.22423	0.19124
C-H ( $C_b H$ )	$C_b$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	76.35	103.65	40.11	1.22423	0.19124
C-H ( $C_c H$ )	$C_c$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	74.42	105.58	38.84	1.24678	0.21379
$N(H)C_a = C_d$	$C_a$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	134.85	45.15	59.72	0.74394	0.57165
$N(H)C_b = C_e$	$C_b$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	134.85	45.15	59.72	0.74394	0.57165
$(H)C_c = C_{\text{Hered}}(H)$	$C_c$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	134.24	45.76	58.98	0.75935	0.55533
$(H)C_d(C_e)C_f = C_{\text{Hered}}$	$C_d$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_a(H)C_d = N$	$C_a$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	128.54	51.46	58.65	0.76572	0.50501
$C_b(H)C_e = N$	$C_b$	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	128.54	51.46	58.65	0.76572	0.50501
$C_c(H)C_f = N$	$C_c$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_d(H)C_e = N$	$C_d$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_e(H)C_f = N$	$C_e$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_f(H)C_g = N$	$C_f$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_g(H)C_h = N$	$C_g$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_h(H)C_i = N$	$C_h$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_i(H)C_j = N$	$C_i$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_j(H)C_k = N$	$C_j$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_k(H)C_l = N$	$C_k$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_l(H)C_m = N$	$C_l$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_m(H)C_n = N$	$C_m$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_n(H)C_o = N$	$C_n$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_o(H)C_p = N$	$C_o$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_p(H)C_q = N$	$C_p$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_q(H)C_r = N$	$C_q$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_r(H)C_s = N$	$C_r$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_s(H)C_t = N$	$C_s$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_t(H)C_u = N$	$C_t$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_u(H)C_v = N$	$C_u$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_v(H)C_w = N$	$C_v$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_w(H)C_x = N$	$C_w$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_x(H)C_y = N$	$C_x$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_y(H)C_z = N$	$C_y$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038
$C_z(H)C_{\text{Hered}} = N$	$C_z$	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	134.81	45.19	59.66	0.74430	0.57038



Table 15.318. The energy parameters (eV) of functional groups of isoquinoline.

Parameters	$\pi$ C=C Group	C-H Group	C-C Group	$\pi$ C=N Group
$f_i$	0.75	1	1	0.75
$n_1$	2	1	1	2
$n_2$	0	0	0	0
$n_3$	0	0	0	0
$C_1$	0.5	0.75	0.5	0.5
$C_2$	0.85252	1	1	0.91140
$C_3$	1	1	1	1
$C_4$	0.85252	0.91771	0.85252	0.91140
$C_5$	0	1	0	0
$C_6$	3	1	2	3
$C_7$	0	1	0	0
$C_{10}$	0.5	0.75	0.5	0.5
$C_{20}$	0.85252	1	1	0.91140
$V_e$ (eV)	-101.12679	-37.10024	-34.43791	-102.01431
$V_s$ (eV)	20.69825	13.17125	10.26723	21.41410
$T$ (eV)	34.31559	11.58941	9.80539	34.65890
$V_m$ (eV)	-17.15779	-5.79470	-4.90270	-17.32945
$E_{\pi}(\pi, \pi)$ (eV)	0	-14.63489	-14.63489	0
$\Delta E_{\pi, \pi^*}(\pi, \pi)$ (eV)	0	-1.13379	-1.13379	0
$E_{\pi}(\pi, \pi)$ (eV)	0	-13.50110	-13.50110	0
$E_{\pi}(\pi, \pi)$ (eV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_{\pi}(\pi, \pi) - \text{atom, nsp}^1, \text{AO}$ (eV)	-2.26759	-0.56690	-0.56690	-1.44915
$E_{\pi}(\pi)$ (eV)	-65.53833	-32.20226	-32.20226	-64.71988
$\omega$ ( $10^5 \text{ rad/s}$ )	49.7272	26.4826	23.6343	43.6311
$E_c$ (eV)	32.73133	17.43132	15.55648	28.71875
$E_b$ (eV)	-0.35806	-0.26130	-0.25127	-0.33540
$E_{\text{kin}}$ (eV)	0.19649	0.35532	0.12312	0.19649
	[49]	Eg. (13.458)	[2]	[49]
$E_{\text{oe}}$ (eV)	-0.25982	-0.08364	-0.18971	-0.23715
$E_{\text{oe}}$ (eV)	0.14803	0.14803	0.14803	0.09457
$E_{\pi}(\pi, \pi)$ (eV)	-49.54347	-32.28590	-32.39198	-48.82472
$E_{\text{kin}}(\pi, \pi)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{kin}}(\pi, \pi)$ (eV)	0	-13.59844	0	0
$E_{\pi}(\pi, \pi)$ (eV)	5.63881	3.90454	3.12220	4.92005



Table 15.319. The total bond energies of isoquinoline calculated using the functional group composition and the energies of Table 15.318 compared to the experimental values [2].

Formula	Name	$\text{C}=\text{C}$	$\text{C}-\text{H}$	$\text{C}-\text{C}$	$\text{C}=\text{N}$	Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$\text{C}_9\text{H}_7\text{N}$	Isoquinoline	8	7	1	2		85.40453	85.44338	0.00046

Table 15.320. The bond angle parameters of isoquinoline and experimental values [1].  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Table 15.320. The bond angle parameters of isooquinoline and experimental values [1]. $E_r$ is $E_r(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ .																									
Atoms of Angle	$2c'$ Bond 1 ( $a_n$ )	$2c'$ Bond 2 ( $a_n$ )	$2c'$ Terminal Atom ( $a_n$ )	$E_r^{\text{calc}}(\text{Atom 1})$	Atom 1 Hybridization Designation (Table 15.3B)	$E_r^{\text{calc}}(\text{Atom 2})$	Atom 2 Hybridization Designation (Table 15.3B)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c'_1$	$E_r$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_l$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cat. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )						
$\angle C'CC$	2.62936	2.65034	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				119.40	119.4						
$\angle C'CH$	2.54147	2.54147	4.3818	-17.63216	22											119.40		120.30	(naphthalene)						
$\angle C'NC'_k$	2.54147	2.54147	4.3818	-17.63216	24	-17.71560	24	0.78050	0.78001	1	1	1	0.77436	-1.85836				119.10							



## INDOLE

Indole having the formula  $C_8H_7N$  comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 74. The aromatic  $C=C$  and  $C-H$  functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The  $CH$ ,  $NH$ , and  $C_d = C_e$  groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The  $C_b - C_d$  single bond of aryl carbon to the  $C_d = C_e$  bond is also a functional group. This group is equivalent to the  $C-C(O)$  group of benzoic acids with regard to  $\Delta E_{H_1MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom - atom, msp^3.AO)$  in Eq. (15.52) both being  $-1.29147 \text{ eV}$ . This energy is a linear combination of  $\frac{-1.13379 \text{ eV}}{2}$ ,  $E_T(atom - atom, msp^3.AO)$  of the  $C-H$  group that the  $C_b - C_d$  and  $C-C(O)$  groups replace, and that of an independent  $C2sp^3 HO$ ,  $-0.72457 \text{ eV}$  (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term  $c_2$  is the aromatic  $c_2(benzeneC2sp^3HO) = 0.85252$  to match the aryl  $C2sp^3 HO$ , and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the  $C-N-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO \text{ to } N) = 0.84665$  (Eq. (15.152)) matches the aromatic character of the  $C2sp^3 HO$ s to the  $N$  atom of the  $NH$  group, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(benzeneC2sp^3HO) = 0.85252$ . Furthermore,  $\Delta E_{H_1MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom - atom, msp^3.AO)$  in Eq. (15.52) are both  $-2.42526 \text{ eV}$  which is a linear combination of  $\frac{-1.13379 \text{ eV}}{2}$ ,  $E_T(atom - atom, msp^3.AO)$  of the  $C-H$  group that the  $C_e - N$  bond replaces, and  $-1.85836 \text{ eV}$  (Eq. (14.513)) which is equivalent to the corresponding component of the  $C-N-C$ -bond of pyrrole.



The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the  
 5 sum over the integer multiple of each  $E_p(\text{Group})$  of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.79-15.108) are given in Table 15.326.

Table 15.321. The symbols of functional groups of indole.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C} = C$
CH (aromatic)	CH (i)
$C_d = C_e$ double bond	$C = C$
$C_b - C_d$	$C - C$
CH	CH (ii)
$C_e - N - C_e$	$C - N - C$
NH group	NH



Table 15.322. The geometrical bond parameters of indole and experimental values [1].

Parameter	C=C Group	C-H (i) Group	C=C Group	C-H (ii) Group	C-C Group	C-N-C Group	NH Group
$a$ ( $a_0$ )	1.47348	1.60661	1.45103	1.53380	1.81395	1.44394	1.24428
$c'$ ( $a_0$ )	1.31468	1.03299	1.30463	1.01120	1.34683	1.30144	0.94134
Bond Length $2c'$ ( $\text{\AA}$ )	1.39140	1.09327	1.38076	1.07021	1.42542	1.37738	0.996270
Exp. Bond Length ( $\text{\AA}$ )	1.399 (benzene)	1.101 (benzene)	1.382 (pyrrole)	1.076 (pyrrole)	1.417 (pyrrole)	1.370 (pyrrole)	0.996 (pyrrole)
$h_a c'$ ( $a_0$ )	0.66540	1.22265	0.63517	1.15326	1.21510	0.62548	0.81370
$e$	0.89223	0.64537	0.89910	0.65928	0.74248	0.90131	0.75653

Table 15.323. The MO to HO intercept geometrical bond parameters of indole.  $R_i$  is an alkyl group and  $R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy $C^{2sp^3}$ (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{total}}(C^{2sp^3})$ Final	$E(C^{2sp^3})$ Final	$\theta'$ ( $^\circ$ )	$\theta_i$ ( $^\circ$ )	$\theta_z$ ( $^\circ$ )	$d_i$ ( $a_0$ )	$d_z$ ( $a_0$ )
$C-H(C'H)$	$C'_a$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C'_a = HC'_a = C'_{a,ke}$	$C'_a$	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$C'_a = (C'_a)C'_a = C'_i$	$C'_a$	-0.85035	-0.64574	-0.85035	0	-153.96212	0.91771	-17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124
$C'_a = C'_i(N)C'_a$	$C'_c$	-0.60631	-0.85035	-0.85035	0	-153.92270	0.91771	-17.13276	-16.94190	134.16	45.84	58.89	0.76140	0.55328
$C'_a = C'_i(N)C'_a$	$C'_a$	-0.85035	-0.85035	-0.64574	0	-153.96212	0.91771	-17.17218	-16.98132	87.89	92.11	40.66	1.37597	0.02914
$C'_a(H)C'_a - C'_a(H)C'_c$	$C'_a$	-0.64574	-1.13379	0	0	-153.39522	0.91771	-16.0528	-16.41442	90.51	89.49	42.40	1.33953	0.00729
$C'_a(H)C'_a - C'_a(H)C'_c$	$C'_a$	-0.64574	-1.13379	0	0	-153.39522	0.91771	-16.0528	-16.41442	137.29	42.71	61.04	0.70255	0.60208
$C'_a(H)C'_a = C'_iN$	$C'_a$	-1.13379	-0.60631	0	0	-153.35580	0.91771	-16.56586	-16.37500	137.37	42.63	61.14	0.70038	0.60425
$C'_a(H)C'_a = C'_iN$	$C'_c$	-1.13379	-0.60631	0	0	-153.35580	0.91771	-16.56586	-16.37500	138.03	41.97	61.42	0.69080	0.61064
$C'_aC'_c - NC'_c$	$N$	-0.60631	-0.60631	0	0		0.93084	-16.03838		139.04	40.96	62.76	0.66083	0.64061
$C'_aC'_c - NC'_c$	$N$	-0.60631	-0.60631	0	0		0.93084	-16.03838		119.52	60.48	65.13	0.52338	0.41796
$N-H(NH)$	$C'_c$	-0.60631	-0.60631	-0.60631	0	-153.92269	0.91771	-17.13276	-16.94189	136.97	43.03	60.05	0.72095	0.58048
$C'_cC'_c - NC'_c$	$C'_c$	-0.85035	-0.85035	-0.60631	0	-153.92269	0.91771	-17.13276	-16.94189					



Table 15.324. The energy parameters (eV) of functional groups of indole.

Parameters	C=C Group	CH (i) Group	C=C Group	C-C Group	CH (ii) Group	C-N-C Group	NH Group
$f_1$	0.75	1	1	1	1	1	1
$n_1$	2	1	2	1	1	2	1
$n_2$	0	0	0	0	0	0	0
$n_3$	0	0	0	0	0	0	0
$C_1$	0.5	0.75	0.5	0.5	0.75	0.5	0.75
$C_2$	0.85252	1	0.85252	1	1	0.85252	0.93613
$C_3$	1	1	1	1	1	1	0.75
$C_4$	0.85252	0.91771	0.85252	0.85252	0.91771	0.84665	0.92171
$C_5$	0	1	0	0	1	0	1
$C_6$	3	1	4	2	1	4	1
$C_7$	0	1	0	0	1	0	1
$C_{10a}$	0.5	0.75	0.5	0.5	0.75	0.5	0.75
$C_{2a}$	0.85252	1	0.85252	1	1	0.85252	1
$V_1$ (eV)	-101.12679	-37.10024	-104.37986	-32.93291	-39.09538	-104.73877	-39.48897
$V_2$ (eV)	20.69825	13.17125	20.85777	10.10210	13.45505	20.90891	14.45367
$T$ (eV)	34.31559	11.58941	35.96751	9.07768	12.74462	36.26840	15.86820
$V_a$ (eV)	-17.15779	-5.79470	-17.98376	-4.53884	-6.37231	-18.13420	-7.93410
$E_1$ (eV)	0	-14.63489	0	-14.63489	-14.63489	0	-14.53414
$\Delta E_{H_{10a}}$ (eV)	0	-1.13379	-2.26759	-1.29147	-2.26758	-2.42526	0
$E_2$ (eV)	0	-13.50110	2.26759	-13.34342	-12.36731	2.42526	-14.53414
$E_3$ (eV)	-63.27075	-31.63539	-63.27075	-31.63539	-31.63533	-63.27040	-31.63534
$E_4$ (eV)	-2.26759	-0.56690	-2.26759	-1.29147	0	-2.42526	0
$E_5$ (eV)	-65.53833	-32.20226	-65.53833	-32.92684	-31.63537	-65.69600	-31.63537
$\omega$ ( $10^5$ rad/s)	49.7272	26.4826	15.4421	21.8249	28.9084	54.5632	48.7771
$E_6$ (eV)	32.73133	17.43132	10.16428	14.36554	19.02803	35.91442	32.10594
$\tilde{E}_7$ (eV)	-0.35806	-0.26130	-0.20668	-0.24690	-0.27301	-0.38945	-0.35462
$\tilde{E}_8$ (eV)	0.19649	0.35532	0.17897	0.12312	0.39427	0.11159	0.40696
$\tilde{E}_{K\alpha}$ (eV)	[49]	$E_0$ (13.458)	[6]	[2]	[56]	[12]	[24]
$\tilde{E}_{\alpha\alpha}$ (eV)	-0.25982	-0.08364	-0.11720	-0.18534	-0.07587	-0.33365	-0.15115
$E_{\alpha\alpha}$ (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\gamma}$ (eV)	-49.54347	-32.28590	-65.77272	-33.11218	-31.71124	-66.36330	-31.78651
$E_{\text{indol}}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{\text{indol}}$ (eV)	0	-13.59844	0	0	-13.59844	0	-13.59844
$E_{\text{indol}}$ (eV)	5.63881	3.90454	7.23317	3.84240	3.32988	7.82374	3.51208



Table 15.325. The total bond energies of indole calculated using the functional group composition and the energies of Table 15.324 compared to the experimental values [2].

Formula	Name	$\nu$ C=C	CH (i)	C=C	C-C	CH (ii)	C-N-C	NH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>8</sub> H <sub>7</sub> N	Indole	6	4	1	1	2	1	1	78.3215	78.314	-0.00010

Table 15.326. The bond angle parameters of indole and experimental values [1]. In the calculation of  $\theta_v$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{usp}^3, AO)$ .

Atoms of Angle	$2c^1$ Bond 1 ( $a_1$ )	$2c^1$ Bond 2 ( $a_1$ )	$2c^1$ Terminal Atom ( $a_1$ )	$E_{\text{conductor}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{\text{conductor}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	$c_2$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$c_1$	$c_1'$	$E_T$ (eV)	$\theta_v$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle C'C'C'$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85336				120.19	120 [50-52] (benzene)
$\angle C'CH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)



## ADENINE

Adenine having the formula  $C_5H_5N_5$  comprises a pyrimidine moiety with an aniline group and a conjugated five-membered ring which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 75. The aromatic  $C=C$ ,  $C-H$ , and  $C=N$  functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The  $NH_2$  and  $C_a-N_a$  functional groups of the aniline moiety are equivalent to those of aniline as given in the corresponding section. The  $CH$ ,  $NH$ ,  $C_d-N_e$ , and  $N_e=C_e$  groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The  $C-N-C$  functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the  $C-N-C$  group bonding to aryl and alkenyl groups.

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.332 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.79-15.108) are given in Table 15.332.

Table 15.327. The symbols of functional groups of adenine.

Functional Group	Group Symbol
$CC$ (aromatic bond)	$C=C$
$CH$ (aromatic)	$CH$ (i)
$C_{b,c}^{3e}=N_c$ $C_{a,b}^{3e}=N_b$	$C=N$
$C_a-N_a$	$C-N$ (a)
$NH_2$ group	$NH_2$
$N_e=C_e$ double bond	$N=C$
$C_d-N_e$	$C-N$ (b)
$N_dH$ group	$NH$
$CH$	$CH$ (ii)
$C_c-N_d-C_e$	$C-N-C$



Table 15.328. The geometrical bond parameters of adenine and experimental values [1].

Parameter	C=C Group	CH (i) Group	C=N Group	C-N (a) Group	NH <sub>2</sub> Group	N=C Group	C-N (b) Group	NH Group	CH (ii) Group	C-N-C Group
$a$ ( $a_0$ )	1.47348	1.60061	1.47169	1.81158	1.24428	1.44926	1.82450	1.24428	1.53380	1.44394
$c'$ ( $a_0$ )	1.31468	1.03299	1.27073	1.34595	0.94134	1.30383	1.35074	0.94134	1.01120	1.30144
Bond Length 2c' (Å)	1.39140	1.09327	1.34489	1.42449	0.99627	1.37991	1.42956	0.996270	1.07021	1.37738
Exp. Bond Length (Å)	1.393 (pyrimidine)	1.084 (pyridine)	1.340 (pyrimidine)	1.431 (aniline)	0.998 (aniline)			0.996 (pyrrole)	1.076 (pyrrole)	1.370 (pyrrole)
$h.c$ ( $a_0$ )	0.66540	1.22265	0.74237	1.21254	0.81370	0.63276	1.22650	0.81370	1.15326	0.62548
$e$	0.89223	0.64537	0.86345	0.74297	0.75653	0.89565	0.74033	0.75653	0.65928	0.90131

Table 15.329. The MO to HO intercept geometrical bond parameters of adenine.  $R_i$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{exp}, \text{AO})$ .

Bond	Atom	$E_T$ (eV) Bond 1	$E_T$ (eV) Bond 2	$E_T$ (eV) Bond 3	$E_T$ (eV) Bond 4	Final Total Energy C2sp <sup>2</sup> (eV)	$r_{\text{final}}$ ( $a_0$ )	$E_{\text{bond}}$ (eV) Final	$E(\text{C2sp}^2)$ (eV) Final	$\theta^*$ (°)	$\theta_i$ (°)	$\theta_j$ (°)	$d_i$ ( $a_0$ )	$d_j$ ( $a_0$ )
$C_1(N_1)C_2(N_2)H-H$	$N_1$	-0.56090	0	0	0	-153.57636	0.93084	-15.39765	-15.39765	121.74	58.26	67.49	0.47034	0.46500
$C_2(N_2)C_3(N_3)H_2$	$C_2$	-0.56090	-0.54343	-0.83035	0	-153.57636	0.91771	-16.78642	-16.78642	89.90	90.10	41.95	1.34737	0.00142
$C_2(N_2)C_3(N_3)H_2$	$N_2$	-0.56090	0	0	0	-153.57636	0.93084	-15.39765	-15.39765	96.32	83.68	46.43	1.28839	0.09756
$C_3(N_3)C_4(N_4)H$	$C_3$	-0.54343	-0.54343	-0.56090	0	-153.26945	0.91771	-16.47951	-16.28865	78.27	101.73	41.39	1.20084	0.16785
$C_3(N_3)C_4(N_4)H$	$C_4$	-0.92018	-0.60631	0	0	-153.15119	0.91771	-16.36125	-16.17038	79.01	100.29	41.89	1.19199	0.15860
$N-H$	$N$	-0.60631	-0.60631	0	0	-153.15119	0.93084	-16.03838	-16.03838	119.52	60.48	65.13	0.32338	0.41796
$C_5(N_5)C_6(N_6)H$	$C_5$	-0.83035	-0.54343	-0.56090	0	-153.57626	0.91771	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50001
$C_5(N_5)C_6(N_6)H$	$N_5$	-0.54343	-0.54343	0	0	-153.57626	0.93084	-15.91561	-15.91561	130.61	49.39	60.97	0.71418	0.35656
$N_5C_5=N_6C_6$	$C_5$	-0.54343	-0.54343	-0.56090	0	-153.26945	0.91771	-16.47951	-16.28865	129.26	50.74	59.44	0.74824	0.32249
$C_5(N_5)C_6(N_6)H$	$C_6$	-0.83035	-0.54343	-0.60631	0	-153.61578	0.91771	-16.82384	-16.63498	128.45	51.55	58.55	0.76792	0.50281
$N_5C_5=N_6C_6$	$C_6$	-0.83035	-0.54343	-0.56090	0	-153.57626	0.91771	-16.78642	-16.59556	134.85	43.15	59.72	0.74304	0.37165
$N_5(N_5)C_6(N_6)C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$C_7$	-0.83035	-0.83035	-0.46459	0	-153.78097	0.91771	-16.09103	-16.80017	134.44	43.56	59.22	0.75398	0.56071
$C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$C_8$	-0.83035	-0.54343	-0.60631	0	-153.61578	0.91771	-16.82384	-16.63498	134.77	45.23	59.62	0.74516	0.56952
$C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$C_9$	-0.83035	-0.54343	-0.60631	0	-153.61578	0.91771	-16.82384	-16.63498	137.54	42.46	60.78	0.70488	0.59656
$N_5(N_5)C_6(N_6)C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$N_6$	-0.60631	-0.60631	0	0	-153.78097	0.93084	-16.03838	-16.03838	139.04	40.96	62.76	0.66083	0.64661
$C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$C_8$	-0.60631	-0.92018	0	0	-153.15119	0.91771	-16.36125	-16.17038	138.42	41.58	61.93	0.67940	0.62303
$C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$C_9$	-0.92018	-0.60631	0	0	-153.15119	0.91771	-16.36125	-16.17038	137.93	42.07	61.72	0.68657	0.61726
$C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$N_7$	-0.92018	-0.46459	0	0	-153.78097	0.93084	-16.21952	-16.21952	138.20	41.80	62.08	0.67849	0.62534
$C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$C_8$	-0.46459	-0.92018	0	0	-153.78097	0.93084	-16.21952	-16.21952	91.32	88.68	43.14	1.33135	0.01939
$C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$	$C_9$	-0.46459	-0.83035	-0.83035	0	-153.78097	0.91771	-16.99103	-16.80017	87.71	92.29	40.72	1.38280	0.03206



Table 15.330. The energy parameters (eV) of functional groups of adenine.

Parameters	$\frac{3\sigma}{C=C}$ Group	CH (i) Group	$\frac{3\sigma}{C=N}$ Group	C-N (a) Group	NH <sub>2</sub> Group	N=C Group	C-N (b) Group	NH Group	CH (ii) Group	C-N-C Group
$f_i$	0.75	I	0.75	I	I	I	I	I	I	I
$n_i$	2	I	2	I	2	2	I	I	I	2
$n_2$	0	0	0	0	0	0	0	0	0	0
$n_3$	0	0	0	0	I	0	0	0	0	0
$C_1$	0.5	0.75	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.5
$C_2$	0.85252	I	0.91140	I	0.93613	0.85252	I	0.93613	I	0.85252
$c_1$	I	I	I	I	0.75	I	I	0.75	I	I
$c_2$	0.85252	0.91771	0.91140	0.84665	0.92171	0.84665	0.84665	0.92171	0.91771	0.84665
$c_3$	0	I	0	0	0	0	0	I	I	0
$c_4$	3	I	3	2	I	4	2	I	I	4
$c_5$	0	I	0	0	2	0	0	I	I	0
$C'$	0.5	0.75	0.5	0.5	1.5	0.5	0.5	0.75	0.75	0.5
$C''$	0.85252	I	0.91140	I	I	0.85252	I	I	I	0.85252
$V_1$ (eV)	-101.12679	-37.10024	-102.01431	-32.76465	-78.97795	-103.92756	-32.44864	-39.48897	-39.09538	-104.73877
$V_2$ (eV)	20.69825	13.17125	21.41410	10.10870	28.90735	20.87050	10.07285	14.45367	13.45505	20.90891
$T$ (eV)	34.31559	11.58941	34.65890	9.04312	31.73641	35.85539	8.89248	15.86820	12.74462	36.26840
$V_3$ (eV)	-17.15779	-5.79470	-17.32945	-4.52156	-15.86820	-17.92770	-4.44624	-7.93410	-6.37231	-18.13420
$E_{ion}$ (eV)	0	-14.63489	0	-14.63489	-14.53414	0	-14.63489	-14.53414	-14.63489	0
$\Delta E_{ion}^{H_{2.216}}$ (no int) (eV)	0	-1.13379	0	-1.13379	0	-1.85836	-0.92918	0	-2.26758	-2.42526
$E_T$ (no int) (eV)	0	-13.50110	0	-13.50110	-14.53414	1.83836	-13.70571	-14.53414	-12.36731	2.42526
$F_1$ (no int) (eV)	0	0	0	0	-14.53414	0	0	0	0	0
$F_2$ (no int) (eV)	-63.27075	-31.63539	-63.27076	-31.63549	-48.73654	-63.27100	-31.63527	-31.63534	-31.63533	-63.27040
$E_T^{atom-atom, imp^3, A(\sigma)}$ (eV)	-2.26759	-0.56690	-1.44915	-1.13379	0	-1.85836	-0.92918	0	0	-2.42526
$F_3$ (no int) (eV)	-65.53833	-32.20226	-64.71988	-32.76916	-48.73660	-65.12910	-32.36455	-31.63537	-31.63537	-65.69600
$\omega$ (10 <sup>12</sup> rad/s)	49.7272	26.4826	43.6311	11.9890	68.9812	15.4704	21.5213	48.7771	28.9084	54.5632
$E_z$ (eV)	32.73133	17.43132	28.71875	7.89138	45.40465	10.18290	14.16571	32.10594	19.02803	35.91442
$\bar{E}_n$ (eV)	-0.35806	-0.26130	-0.33540	-0.18211	-0.42172	-0.20558	-0.24248	-0.35462	-0.27301	-0.39845
$\bar{E}_{nvb}$ (eV)	0.19649	0.35532	0.19649	0.15498	0.40929	0.20768	0.12944	0.40696	0.39427	0.11159
$\bar{E}_{nvb}$ (eV)	[49]	E <sub>q</sub> (13.458)	[49]	[54]	[22]	[58]	[23]	[24]	[56]	[12]
$\bar{E}_{nc}$ (eV)	-0.25982	-0.08364	-0.23715	-0.10462	-0.21708	-0.10174	-0.17775	-0.15115	-0.07587	-0.33365
$E_{avg}$ (eV)	0.14803	0.14803	0.09457	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_z^{functional}$ (eV)	-49.54347	-32.28590	-48.82472	-32.87379	-49.17075	-65.33259	-32.74230	-31.78651	-31.71124	-66.36390
$E_{total}^{functional}$ (no int) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
$E_{ionization}$ (no int) (eV)	0	-13.59844	0	0	-13.59844	0	0	-13.59844	-13.59844	0
$E_{ionization}$ (eV)	5.63881	3.90454	4.92005	3.60401	7.43973	6.79303	3.47253	3.51208	3.32988	7.82374

Table 15.331 The total bond energies of adenine calculated using the functional group composition and the energies of Table 15.330 compared to the experimental values [2].

Table 15.331. The total bond energies of adenine calculated using the functional group composition and the energies of table 15.330 compared to the experimental values (2).

Formula	Name	$\text{C}=\text{N}$ $\text{C}=\text{C}$	$\text{C}-\text{N}$ (a) $\text{C}=\text{C}$	$\text{NH}_2$ Group	$\text{N}=\text{C}$ $\text{C}-\text{N}$ (b)	$\text{NH}$ $\text{C}-\text{N}-\text{C}$	CH (ii)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>44</sub> N <sub>4</sub>	Adenine	7	4	1	1	1	1	70.83735	70.79811	-0.00055



Table 15.332. The bond angle parameters of adenine and experimental values [61]. In the calculation of  $\theta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_T(atom - atom, msp, AO)$ .

Atoms of Angle	$\angle C_1$ Bond 1 ( $a_1$ )	$\angle C_2$ Bond 2 ( $a_2$ )	$\angle C_3$ Terminated Atom ( $a_3$ )	$E_r$ Terminated Atom 1 ( $a_1$ )	Atom 1 Hybridization Designation (Table 15.3B)	$E_r$ Terminated Atom 2 ( $a_2$ )	Atom 2 Hybridization Designation (Table 15.3B)	$c_1$ Atom 1	$c_2$ Atom 2	$C_1$	$C_2$	$C_3$	$c_1$	$c_2$	$E_r$ (eV)	$\theta_r$ ( $^\circ$ )	$\theta_1$ ( $^\circ$ )	$\theta_2$ ( $^\circ$ )	Cal. $\theta$ ( $^\circ$ )	Exp. $\theta$ ( $^\circ$ )
$\angle HNH$	1.88268	1.88268	3.1539	-14.53414	N	H	H	0.95613 (Eq. (15.248))	1	1	1	1	0.75	1.06823	0				113.89	113.9 [1] (equiline)
$\angle HNC$	1.88268	2.69190	4.0497	-14.53414	N		6	0.84665 (Eq. (15.152))	0.84665 (Eq. (15.152))	0.75	1	1	0.75	1.01912	0				123.60	118
$\angle HNC$	2.06598	2.54147	3.9497	-14.52575	I		N	0.91771 (Eq. (15.116))	0.91771 (Eq. (15.116))	0.75	1	1	0.75	0.99312	0				117.65	115 116
$\angle HNC$	2.02241	2.60766	4.0661	-16.36125	10		N	0.83159 (Eq. (15.152))	0.83159 (Eq. (15.152))	0.75	1	1	0.75	1.01811	0				122.35	126
$\angle HNC$																	122.35	112.64	125.02	119
$\angle HNC$	1.88268	2.60287	4.0497	-14.53414	N		6	0.84665 (Eq. (15.152))	0.84665 (Eq. (15.152))	0.75	1	1	0.75	1.01912	0				128.35	127
$\angle HNC$	2.60766	2.60287	4.3359	-16.21952	8		7	0.83885 (Eq. (15.116))	0.84833 (Eq. (15.152))	1	1	1	1	0.84359	-1.44915				112.64	114.4
$\angle HNC$	2.54147	2.60287	4.6260	-14.53414	N		N	0.91771 (Eq. (15.116))	0.84665 (Eq. (15.152))	1	1	1	1	0.87902	-1.44915				128.11	127.8
$\angle HNC$	2.54147	2.54147	4.5826	-15.55033	3		3	0.87495 (Eq. (15.152))	0.87495 (Eq. (15.152))	1	1	1	1	0.87495	-1.44915				128.75	128.9
$\angle HNC$	2.54147	2.69190	4.5826	-15.91261	5		2	0.85303 (Eq. (15.152))	0.88392 (Eq. (15.152))	1	1	1	1	0.86947	-1.44915				122.22	119.7
$\angle HNC$	2.70148	2.62936	4.3818	-14.53414	N		6	0.84665 (Eq. (15.152))	0.85252 (Eq. (15.152))	1	1	1	1	0.84958	-1.44915				110.56	110.4
$\angle HNC$	2.60287	2.62936	4.1952	-14.53414	N		16	0.84665 (Eq. (15.152))	0.80076 (Eq. (15.152))	1	1	1	1	0.82371	-1.44915				106.60	105.9
$\angle HNC$	2.54147	2.62936	4.4721	-14.53414	N		16	0.91771 (Eq. (15.116))	0.80076 (Eq. (15.152))	1	1	1	1	0.85608	-1.44915				110.73	126.4
$\angle HNC$	2.54147	2.62936	4.4721	-14.53414	N		16	0.91771 (Eq. (15.116))	0.80076 (Eq. (15.152))	1	1	1	1	0.85608	-1.44915				110.73	118.2
$\angle HNC$	2.69190	2.62936	4.5607	-14.53414	N		12	0.91771 (Eq. (15.116))	0.83327 (Eq. (15.152))	1	1	1	1	0.86734	-1.44915				117.97	122.1
$\angle HNC$	2.70148	2.62936	4.8990	-14.53414	N		1	0.91771 (Eq. (15.116))	0.91771 (Eq. (15.116))	1	1	1	1	0.91456	-1.44915				133.55	132.8
$\angle HNC$	2.70148	2.60766	4.2661	-17.92022	28		28	0.75924 (Eq. (15.152))	0.75924 (Eq. (15.152))	1	1	1	1	0.75924	-1.85836				106.93	103.5
$\angle HNC$	2.60287	2.60287	4.2661	-17.75502	25		25	0.76631 (Eq. (15.152))	0.76631 (Eq. (15.152))	1	1	1	1	0.76631	-1.85836				110.07	106.1
$\angle HNC$	2.54147	2.54147	4.3889	-17.40869	21		25	0.78155 (Eq. (15.152))	0.76631 (Eq. (15.152))	1	1	1	1	0.77393	-1.85836				118.09	111.3
$\angle HNC$	2.54147	2.54147	4.3704	-17.71560	24		21	0.76801 (Eq. (15.152))	0.78155 (Eq. (15.152))	1	1	1	1	0.77478	-1.85836				118.59	118.6
$\angle HNC$	2.62936	2.62936	4.4721	-17.71560	24		19	0.76801 (Eq. (15.152))	0.79340 (Eq. (15.152))	1	1	1	1	0.78071	-1.85836				116.52	116.7



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While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.